

Municipal Solid Waste Conversion to Energy and Derived Chemicals using Pyrolysis

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Abstract

This research work evolved through the variables such as time and temperature to determine the highest bio-oil yields. Conventional pyrolysis was adopted in a drop type CVD pyrolyzer given the highest oil yields 32.50 %wt, at 500 °C for 30 min. The bio-oil properties (CHNS-O) at various temperatures were evaluated. Carbon, hydrogen, Nitrogen, sulphur and calorific values were observed to increase as the temperatures increases, having highest values at 500 °C with a sudden decline at 550 °C. While oxygen, water contents, densities and pH values decreases as the temperature increases, with lowest values recorded at 500 °C and sharp increase at 550 °C. Hence, the degrees of de-oxygenation also increases as the temperature increases with 18.87 %wt. at 500 °C and decreased at 550 °C. The results of FTIR analysis of the bio-oils at 500 °C indicate functional groups such as alkyl/Aromatic substitute ether (C-O), Aromatic 1^o amine (C-N), Phenol/3^o Alkanol (O-H), alkenes (C=C), Nitriles (C-N) and amines (N-H) with their areas.

Keywords: Pyrolysis, Bio-oil, Derived chemical, Energy

1. INTRODUCTION

Back in ages, the amounts of waste generated by humans were insignificant due to low population density and low societal level of natural resource exploitation. Common wastes produced at these times were mainly ashes and human biodegradable waste, and these were sent back to the ground locally to decompose with minimum environmental impact (Wikipedia, 2014). However, with the onset of industrialization and the sustained urban growth of large population centres, the build-up of waste in the cities caused a rapid deterioration in the levels of sanitation and general quality of urban life (Wikipedia, 2014). These enormous increase in the quantum and diversity of waste material and their potential harmful effects on the general environment and public health calls for a pressing need to better waste management methods in which the treatment and handling can led to safe disposal, cleaner and healthier environment with sustainable use of the earth's resources (Salman, 2009). Also couple with the demand for fuel and various chemicals increasing day by day, the country has been spending lot on refining petroleum and related products putting pressure on the conventional sources of energy which have been depleting at an alarming rate and hence the focus on alternative renewable source of energy. As a result of these twin reasons, biomass as a renewable energy source has continued to attract more attention and a lot of research in this area is in progress using different solid biomass as the feed material (Islam *et al.*, 2010). Needless to say, municipal solid waste (MSW) is a common waste management problem with biomass obtained from any city area of all over the world as well as in Nigeria. Although for many years, opposition to the use of MSW as an energy resource has been nearly universal among activists and regulators. This opposition has been largely based on bad experiences with traditional garbage incineration facilities, which are associated with high levels of toxic emissions, as well as the perception that using MSW for energy will compete with recycling efforts. But for growing climate, energy, and environmental concerns, coupled with technological developments and regulatory changes has ignited a new interest in MSW as an energy source with the potential to provide renewable energy while reducing greenhouse gas emissions and the need for landfill space (Brian G. and Justin M., 2009). Thus, pyrolysis may be considered as a promising option for resource recovery from MSW, which are abundantly available to produce quality bio-oils. It is therefore, a great potential in converting solid wastes which are very difficult and costly to manage into fuels and chemicals, reducing waste management cost. Due to the low contents of sulphur and nitrogen utilization of the derived energy, it does not add sulphur dioxide, nitrogen oxides and no net carbondioxide, which are greenhouse gases to the atmospheric environment, in contrast to fossil fuels (Ani and Islam, 1997). These also addressed an economical and ecological solution of transforming abundant naturally available materials into something useful to the humanity. Considering the above advantages, this research work was undertaken to produce renewable energy and deriveable chemicals from MSW using pyrolysis. According to daily assessment report of Niger State Environmental Protection Agency (NISEPA) 300 to 400 tons of MSW are generated daily on an average from Minna metropolitan area, this is a great potential for renewable energy conversion and derieved chemicals. Although, these wastes are mostly mixture of substances whose constituents widely varies on location. Thus, sorting is required to classified them into groups and their composition such as organic food wastes, papers, broken glasses and ceramics, metals, plastics, rubber and leather, textiles, wood, yard wastes, others. The organic solid wastes that are lignocellulosic biomass were the target raw materials in this experiment.

RESEARCH METHOD

2.1 Feedstock preparation

The MSW used in this study was obtained from Kampalla dump site of Niger state environmental protection

agency (NISEPA). The site covered about 20 hectares of lowland area of Maikunkele along Minna – Zungeru road; headquarter of Bosso local government area of Niger state on latitude 54° W and longitude 108° S. The heterogeneous mixture of the wastes were sorted and separated out. The residues which were lignocellulosic material (papers, wood, yard trim and food wastes) were taken as the feedstock as shown in figure 2. Prior to pyrolysis, some of the wastes were shredded while others passed through a high speed rotary cutting mill and then sieved to obtain the required particle size of 1.75 mm, then dried to 10 wt. % moisture in an electrical oven for 24 hrs at 105° C. The proximate analysis of MSW was performed to measure the moisture content, ash content, fixed carbon contents and volatile matter using the TGA method. The ultimate analysis was carryout using analytical (Liebig's and Kjeldahl's) method of elemental analysis to determine properties of MSW, which mainly consisted of CHNS, while oxygen contents were determined using calculation difference.

$$O=100-(C\%wt. - H\%wt. - N\%wt. - S\%wt.) \quad (1)$$

The moisture content of MSW was measured through proximate analysis, while the caloric values (HHV) were calculated from the elemental and ash analysis based on Channiwala and Parikh's formula as shown in the following equation (Lim *et al.*, 2014).

$$HHV=0.3491C+1.1783H-1054O-0.0151N+0.1005S-0.0211A \quad (2)$$

Hence, O/C and H/C ratios were calculated as shown in table 1

2.2. Pyrolysis experiment

2.2.1. Apparatus

Figure 1 shows the schematic diagram of a batch type vacuum pump reactor called chemical vapour depositor (CVD) used to carry out the non-catalytic and catalytic Conventional pyrolysis of MSW for the present study. The experimental setup consists of a cylindrical reactor made up of horizontal glass (borax) tube furnace with length-1010mm, internal diameter-60mm and outer diameter-65mm. The pyrolyzer was installed inside an electrical heater and was insulated to enable the heating of the reactor up to 1200° C. The reactor is equipped with a biomass holder (cubit) and connected to both vacuum and nitrogen source. To record the pyrolysis temperature, a K-type thermocouple was inserted inside the pyrolyzer. The pyrolyzer was connected to ice-trap immersed in ice-water bath to condense the pyrolysis vapours at $0-5^{\circ}$ C. The outlet of the ice-trap was connected with the gas sampling bag to collect the non-condensable gases.

2.2.2. Procedure

Conventional pyrolysis was adopted in all the experiments with 20g of MSW loaded into the cubit and fixed into the reactor. A vacuum pump was set to obtained high vacuum inside the pyrolyzer between 0.003 to 0.001 mmHg pressures (< atmospheric pressure). The experiments were carried out in two series. The first part was to determine the effect of time and temperature on products yield (as controls). The temperature of the pyrolyzer was then set between $400-550^{\circ}$ C with intervals of 50° C for the range of periods 10 – 40min with constant heating rate of 20° C/min and N_2 flow rate of 50 ml/min. The duration of the experiments were held at these temperatures until there is no significant gas observed to be released and the CVD reactor automatically terminated at that period. Same procedures were repeated for 20, 30, and 40 min. To evaluate the impact of adding catalyst on pyrolysis condition; the second part of the experiments were performed at the best temperature of 500° C and time 30 min that gives the highest oil yield for non-catalytic pyrolysis by mixing the catalyst to biomass ratio of 0.2–1. In catalytic experiments, the biomass and catalyst were mixed before been inserted into the reactor. In both cases; the pyrolysis process resulted in char, bio-oil and gas products. The fluid gas comes out through the vacuum line of the pyrolyzer and the solid char remain in the cubit as residue. The fluid from the pyrolyzer was then cool through the condenser. The condensate (bio-oil) was collected and stored in a sample bottle for further analysis, while the non-condensate gas was given off as syngas. Mass balance calculations were used to estimate yield; char (wt. %) + bio-oil (wt. %) + gas (wt. %) = 100. Yields of char and bio-oil were determined based on change in weight of the reactor and the condenser respectively, before and after the experiment. The mass of liquid and solid are given within the experiment error of $<\pm 2$.

2.2.3. Analysis of pyrolysis products

After each of the several pyrolysis experiments; the products obtained were bio-char, bio-oil and syngas base on their mass percentages. The bio-oil was found to be in a single phase dark brown colour with a distinct odour similar to smoke from a wood fire and was quite pungent. The pyrolysis oils obtained at pyrolysis temperature of 500° C for 30 min were characterized using the following methods. The proximate and ultimate analyses of bio-oils were performed using the analytical methods. The elemental analysis of the bio-oils were determined through Liebig's, and Kjeldahl's methods of estimating CHNS-O and their high heating values calculated by difference using equation 2. The moisture contents of the bio-oils were determined through proximate method due to unavailability of Karl-Fischer (KF) moisture analyzer which gives better results (Naqvi *et al.*, 2010). According to Brown this analytical procedure is more useful for evaluating bio-char than bio-oils, because the "moisture" and "volatiles" determined are not directly applicable to bio-oil because of the many compounds that volatilize over a wide range of temperatures (Brown J. N., 2009). The FTIR analysis was performed to determine

functional groups at the best operating temperature. The pH value was obtained by a pH probe with a digital meter. The densities were calculated by mass/volume ratio in the lab. According to Naqvi, a formula to estimate the degree of de-oxygenation was proposed by Zabeti as:

$$\text{Degree of deoxygenation} = \left(1 - \left(\frac{[O]_{\text{bio-oil}}}{[O]_{\text{biomass}}} \right) \right) \times 100 \quad (3)$$

Where [O] is oxygen content (mass)

Degree of de-oxygenation is used to judge the amount of oxygen that has been rejected from the biomass and retained in the bio-oil, (Naqvi et al., 2014).

2.3. Figures and Tables

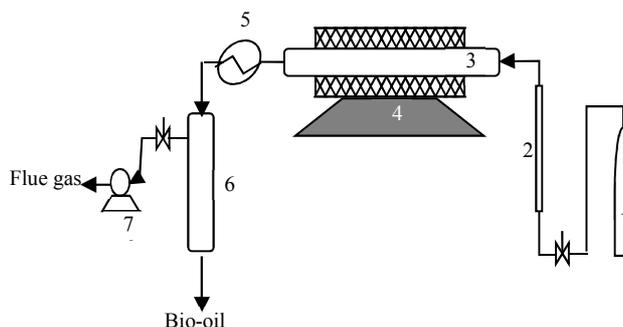


Figure 1: Layout of the pyrolysis process

1-Gas Cylinder, 2-Flow meter, 3.-Glass pyrolyser, 4-Reactor Controls, 5-Coolant, 6-Condenser, 7-Suction Pump.

3. FINDINGS AND DISCUSSION OF RESULTS

3.1. Analysis on feedstock

The heterogeneous nature of the different materials involved in MSW made it nearest to impossible, to use it as raw material for this study. This was due to presence of metals, broken glasses and ceramics. After the raw materials were manually sorted and separated into their various compositions; out of 1 kg of the raw sample collected 71.7g of it contains lignocellulosic materials as demonstrated in figure 2.

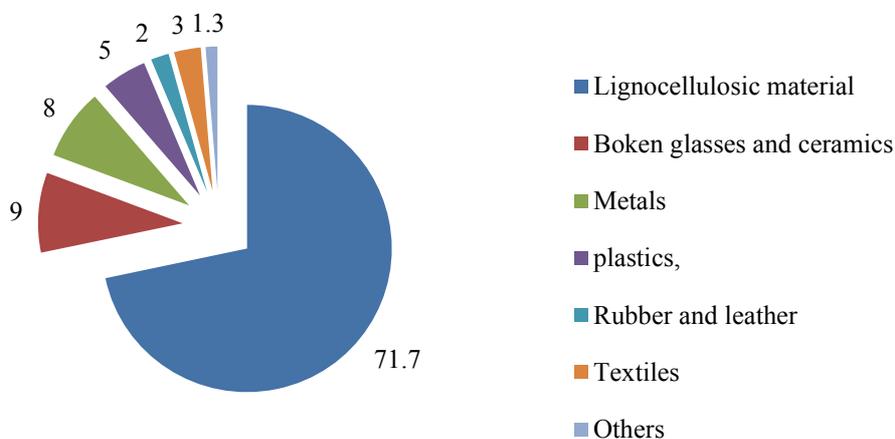


Figure 2: Compositions in 1 kg sample of MSW

The major components of the lignocellulosic material in 71.7g of MSW are shown in figure 3.

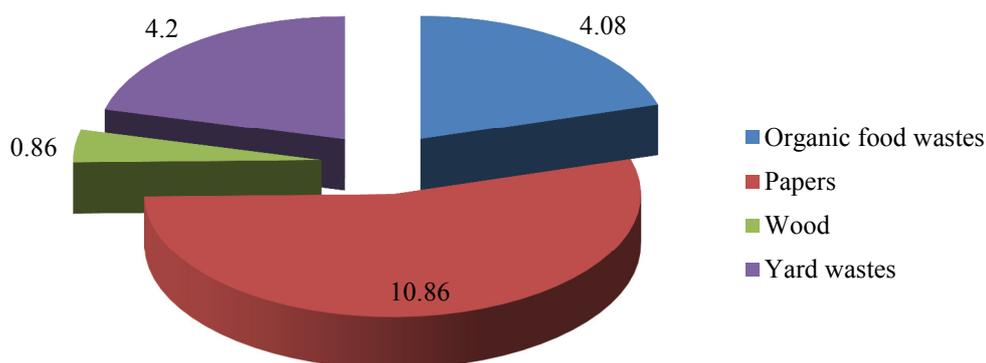


Figure 3: Component of lignocellulosic material in 71.7g of sample MSW

3.1.1. Thermal gravimetric analysis:

TGA4000 was used to determine the mass change of a sample with increasing temperature and time. This data is used for the proximate analysis of biomass, which gives the percent weight of moisture, volatiles, fixed carbon and ash contents. The result is as shown in figure 4 and Table 1.

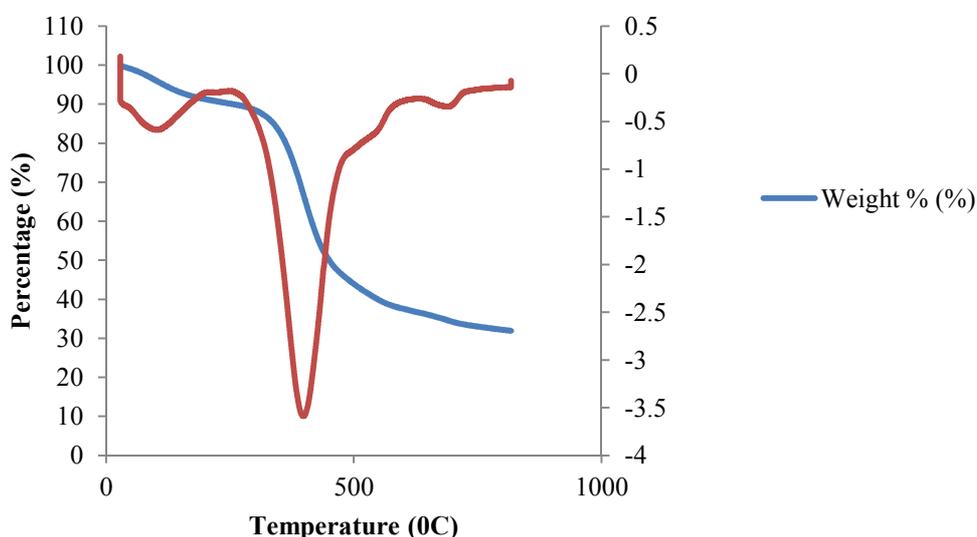


Figure 4: Thermo-Gravimetric Analysis of MSW

Table 1: Proximate analysis from TGA weight loss thermogram and ultimate analysis of MSW

Properties	MSW
Proximate analysis	
Moisture (%)	8.087
Ash (%)	1.612
Volatile component (%)	54.141
Combustible matter (%)	36.160
Ultimate Analysis	
C (%)	31.92
H (%)	09.06
O (%)	47.05
S (%)	1.76
N (%)	0.40
Ash content (%)	1.05
Caloric value (MJ/kg)	17.01
O/C (molar ratio)	1.11
H/C (molar ratio)	3.38
Empirical formula	$CH_{3.38}O_{1.11}N_{0.0107}S_{0.0206}$

3.2. Analysis of pyrolysis products

3.2.1. Effect of time on oil yields

To determine the effect of time on oil yields, series of experimental pyrolysis were performed as control at constant time of 10, 20, 30 and 40 min between the of 400–550 °C, respectively. The best time of 30 min determined to produce the highest oil yield of 32.50 %wt. at temperature of 500 °C as shown in figure 5, and this was used as the base line for catalytic pyrolysis experiment.

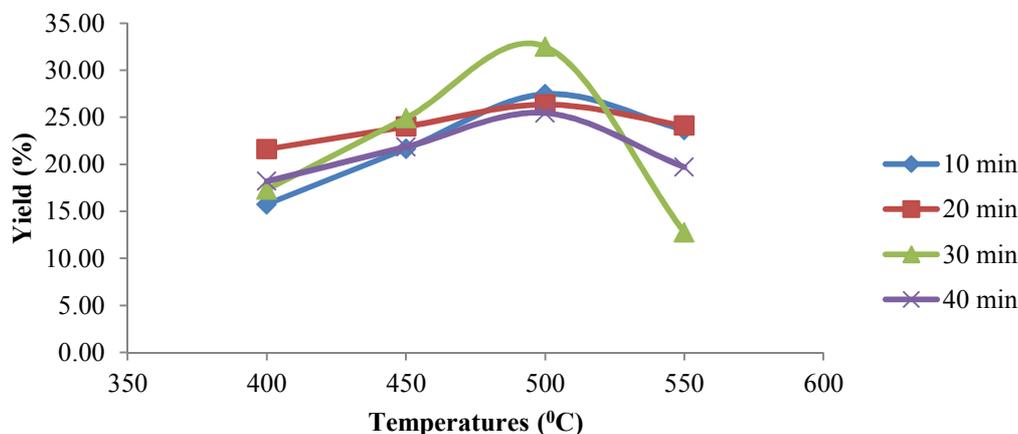


Figure 5: Effect of constant pyrolysis time on oil yields at various temperatures

3.2.2. Impact of temperature on product yields

It is a well established fact that the main parameter among the operating factors is the temperature; hence the impact of pyrolysis temperature on products yields was investigated as illustrated in figure 6. The pyrolysis experiments performed at the various temperatures of 400–550 °C with intervals of 50 °C shows an increased in the bio-oil yields and then decreased at 550 °C. The highest bio-oil yield of 32.50 %wt. was recorded at the pyrolysis temperature of 500 °C and taken to be the best temperature. At temperatures lower than 500 °C the oil yield was less and char yield was more. On the other hand, at temperature higher than 500 °C, the char yields was found to be less with less oil yield; however the gas yield was observed to be higher. The reason for less oil yield at lower temperatures (<500 °C) may be due to insufficient energy to attain complete pyrolysis thereby yielding less oil and more char. On the contrary, the gaseous products obtained at higher temperature (>500 °C) may be attributed to the secondary cracking of the pyrolyzed vapour and decomposition of the bio-char, which lower oil. This agrees with the previous work conducted by other researchers, (Naqvi *et al.*, 2014 and Salman, 2014). From these results, further increase in the temperature could reject more oxygen but failed to improve the quality of bio-oils in terms of higher carbon and lesser oxygen content.

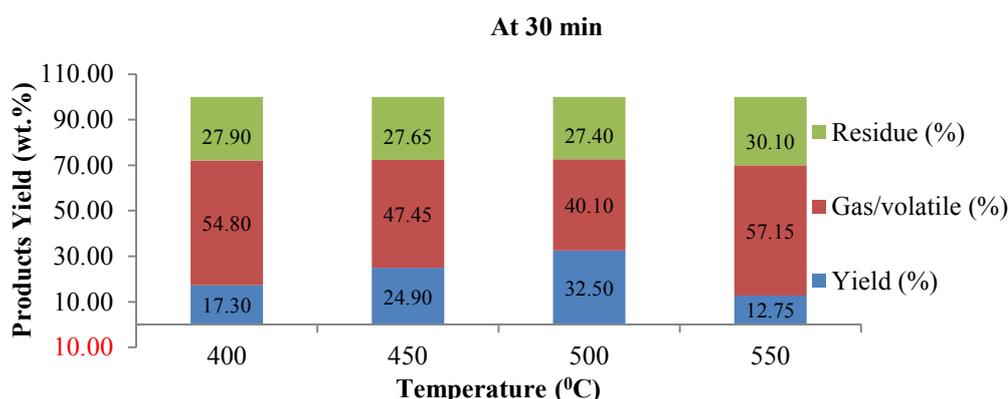


Figure 6: Impact of temperatures on products yield

According to Brown and Naqvi *et al.*, the gases formed during pyrolysis experiments comprises of H₂, CH₄, CO and CO₂ (Brown J. N, 2009 and Naqvi *et al.*, 2014). These gases were used to calculate the compositions (vol. %) as the temperature varies as shown in Table 2. The total gas yields at 500 °C is 40.10 wt. % and with the increase temperature to 550 °C increases to 57.94%wt. while below 500 °C decreases to 47.45%wt. at 450 °C and 54.80%wt. at 400 °C, respectively.

Table 2: Composition of gases (Vol. %) for non-catalyst and catalyst

Gases	400	450	500	550
H ₂	1.22	1.05	0.89	1.27
CH ₄	9.74	8.44	7.13	10.16
CO	17.05	14.76	12.48	17.78
CO ₂	26.79	23.20	19.60	27.94
Total	54.80	47.45	40.10	57.15

The temperatures have different abilities to deoxygenate undesirable constituents of bio-oil to form H₂, CH₄, CO and CO₂. It can be seen that the volume of the gases were decreasing as the temperature increases and has lowest value at temperature of 500 °C as compared to others. This indicate that 500 °C is the moderate temperature of de-oxygenation of harmful oxygenates achieved by converting the gases to less products. The decrease in the volume of the gases as temperature increases to 500 °C, also indicates the inability of the temperatures to de-oxygenate harmful oxygenates and was improved at 500 °C.

3.3. Analysis of the oil yield

3.3.1. Thermo-physical properties of bio-oil

The key bio-oil properties obtained varies with pyrolysis temperatures as depicted in table 3. It appeared dark brownish free from visible sediments; highly acidic with high water content, low heating value and very low sulphur content. The ash content in the oil is very negligible which agrees with other research conducted by (Naqvi *et al.*, 2014). The sulphur contents of the bio-oil produced, was relatively lower than petroleum fuels. The low sulphur contents are positive property for application as fuel. Compared with all pyrolysis temperatures, the bio-oil produced at the 500 °C had higher Carbon (23.70%wt.), Hydrogen (11.20%wt.), Sulphur (0.10%wt.), Nitrogen (1.86%wt.) and lower energy density (16.29%wt) than others as shown in table 4. The nitrogen content is greater than petroleum at the best pyrolysis temperature and is not favourable due to causing NO_x emission in fuel use. These results imply that the bio-oils should be de-nitrogenated to improve their applicability as fuel. The lower heating value of the oil is due to high water content and presence of carbonyl compounds. These results agreed with an earlier study by (Islam *et al.*, 2014), (Naqi., *et al.*, 2014 and Kim *et al.*, 2014).

Table 3: Properties of bio-oil yields

Elements		400	450	500	550
Carbon	(%wt.)	20.49	23.81	24.70	23.50
Hydrogen	(%wt.)	10.64	11.90	12.20	11.48
Sulphur	(%wt.)	0.05	0.07	0.10	0.08
Nitrogen	(%wt.)	0.24	0.46	1.86	0.15
Oxygen	(%wt.)	40.83	39.80	38.97	40.45
Ash content	(%wt.)	0.97	0.96	0.17	0.87
Water contents	(%wt.)	26.78	26.49	26.89	25.47
HHV ^b	(MJ/kg)	15.37	16.29	17.43	15.93
Acidity (pH) at 28.8 °C		3.36	3.39	3.42	3.34
Density (kg/m ³) at 25 °C		1000	892	788	835

The density and oxygen content decreases as the pyrolysis temperatures increases from 400–500 °C, and at 500 °C the bio-oil has minimum values as demonstrated in table 4. Compared with petroleum standard the minimum oxygen content is higher in the bio-oil which results in acidic, unstable and corrosiveness with relatively low energy density. The varying quantities of water formation which forms a stable single-phase mixture decreasing as the temperature also increases, ranging from 26.78, 26.49, 26.89 to 25.47 %wt. water. The high water content of bio-oil is due to formation of water in pyrolysis process. These all agrees with the early study by Naqvi *et al.*, (2014).

In all experiments, the bio-oils consisted of higher acidity (pH) values and decreases as the temperatures increases, while at 500 °C it recorded the lowest acidity (pH) value (3.42) as shown in table 4. This value is lower than 4 indicating it's corrosive nature and resulted from high oxygen content.

3.3.2. Impact of temperature on the degree of de-oxygenation of bio-oil

The degree of de-oxygenation of bio-oil at various pyrolysis temperatures are shown in figure 7. This aimed at reducing the oxygen content of biomass through various pyrolysis temperatures to get high quality bio-oil. It focuses on how much oxygen has been removed from biomass and retained in the bio-oil.

At temperatures below 500 °C, the oxygen removal was less compared to at 500 °C. Higher temperatures helped to remove more oxygen from the original biomass. The results showed that more oxygen is been removed ~18.87%wt at 500 °C as compared to ~13.22%wt. 400 °C, ~16.47%wt. 450 °C, and ~14.03%wt. at 550 °C pyrolysis temperature. It was also observed that the oxygen in the biomass was removed mostly as H₂O and as CO₂/CO.

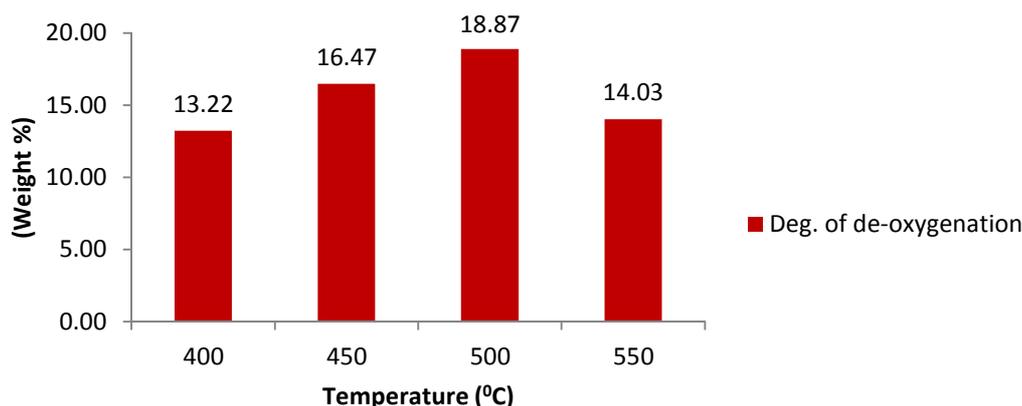


Figure 7: Degree of de-oxygenation of bio-oil

3.3.3 Impact of Temperature on the composition of bio-oil

The bio-oil is a mixture of different compounds and reflects the decomposition of the lignocellulosic content of MSW. To understand how temperature of 500 °C influences the pyrolysis of MSW; the functional groups present in the bio-oils were analyzed using FTIR as shown in figure 8.

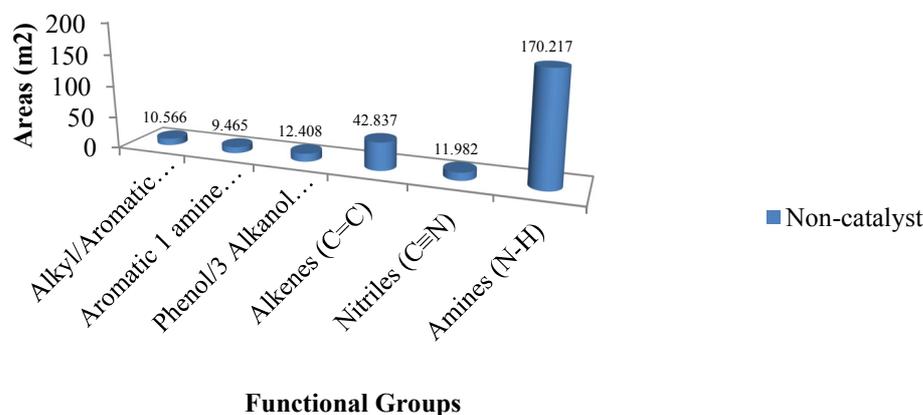


Figure 8: Functional groups of bio-oils and their areas at 500 °C

From figure 8, the functional groups and areas of the bio-oil revealed the different components of MSW with nitrogen-containing compounds and complex carbohydrates. This may suggest that food waste component of MSW contains high source of amino acid (high crude protein). At pyrolysis temperature of 500 °C, where the degree of de-oxygenation is maximum; carboxylic oxygenates are formed through de-carboxylation of organic acids (such as acetic, formic, fatty and amino acids) from cellulose, hemicelluloses, esters and nitrogen-containing compounds (e.g. RCOOH ---- RH + CO₂). Insignificant de-carbonylation of aldehyde, phenol, ketones and carbohydrates compounds also occurred to form aliphatic and aromatic hydrocarbons this is usually catalyzed by metal complexes in the bio-chars. Amines are also formed through depolymerization of amino acids (protein and amides), catalytic hydrogenation of nitriles groups (R-C≡N) and nitro-alkanes (CH₃-CH-NH₂). The areas of the functional groups are 10.566m² alkyl/aromatic substitute ether (C-O), 9.465m² aromatic 1^o amine (C-N), 12.408m² phenol/3^o alkanol (O-H), 42.837m² Alkenes (C=C), 11.982m² nitriles (C≡N) and 170.217m² amines (N-H).

CONCLUSION

MSW pyrolysis is good means of converting waste to clean energy production and chemical extract which can be used in the production of polymers, pharmaceuticals, solvents and food additives. Meanwhile, from the results of FTIR analysis of bio-oils at 500 °C, the carbonyl and acidic components that cause instability and acidity can be catalytically upgraded to diesel and gasoline fuels which can be blended with similar products of fossil fuel to improve the quality and volume of the fuel. This will in turn reduced over dependence on the conventional fuels, increase foreign exchange earnings and creates job opportunities. The presence of amines group may likely be from amino acid and amides in the food wastes which make it unfavourable due to emission of NO_x for the oil use. Thus, food wastes can be isolated from the feedstock or better still further study may be revealed an efficient way of nitrogen removal in the bio-oil in consideration to a specific fuel use.

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