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Valorization of Napier Grass *via* Intermediate Pyrolysis: Optimization Using Response Surface Methodology and Pyrolysis Products Characterization

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Abstract

This study presents first optimization report on pyrolysis oil derived from Napier grass. Effects of temperature, heating rate and nitrogen flow rate on the intermediate pyrolysis of Napier grass biomass in a vertical fixed-bed tubular reactor were investigated collectively. Response surface methodology with central composite design was used for modelling the process and optimization of the process variables. Individual second order polynomial model was found to be adequate in predicting bio-oil, bio-char and non-condensable gas yield. The optimum bio-oil yield of 50.57 wt% was recorded at 600 ^oC, 50 ^oC/min and 5 L/min nitrogen flow. The bio-oil obtained throughout this study was two-phase liquid, organic and aqueous phase. The bio-oil, bio-char and non-condensable gas were characterized using standard analytical techniques. The results revealed that the organic phase consists of hydrocarbons and various benzene derivatives, which can be further processed into fuels and valuable chemicals. The aqueous phase was predominantly water, acids, ketones, aldehydes and some phenolics and other water-soluble organics. The non-condensable gas was made up high hydrogen/carbon monoxide ratio suitable for liquid fuel synthesis via Fischer-Tropsch Synthesis. The bio-char was a porous carbonaceous material with high energy content, which can be applied as a solid fuel, adsorbent or source of biofertilizer. This study demonstrated that Napier grass biomass is a viable feedstock for production of high-value bioenergy precursors.

Keywords: Napier grass; pyrolysis; optimization; Response surface methodology; bio-oil characterization

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1. Introduction

Lignocellulosic biomass such as forest residues, agro-wastes, energy grasses, aquatic plants, algae, continues to again attention as a suitable alternative energy source. They are non-food materials and consist carbon, which can be converted into high-grade fuel or fuel precursor, biochemicals and other valuable product (Mohammed et al., 2016a; 2016b). However, biofuel from these materials is generating another concern. The issue regarding land use, water and other productive resources for the cultivation of such crops instead of food crops are seen as a potential food scarcity. To address these challenges, production of second generation biofuels should be carefully synchronized to encourage more food production in order to develop a sustainable bioenergy system.

Napier grass (*Pennisetum purpureum*) also known as elephant grass, Uganda grass. It is an underutilized herbaceous plant, which can be cultivated up to four times in a year with a ratio of energy output to the energy input of around 25:1 and high biomass yield between 25 and 35 oven dry tons per hectare annually, which corresponds to 100 barrels of oil energy equivalent per hectare (Samson et al., 2005; Flores et al., 2012). Comparing with other energy grasses such as

Miscanthus, switchgrass, the biomass yield is between 10 and 20 oven dry tons per hectare per annum and require some nutrient input during cultivation (Richter et al., 2008; Cadoux et al., 2012). Flores et al. (2012) reported that Napier grass can be grown without any nutrient or fertilizer input. They evaluated the performance of two Napier grass species with and without application of nitrogen fertilizer under the Cerrado climatic condition (semi-humid tropical climate). Their findings revealed that the biomass yield was between 30 to 42 oven dry tons per hectare and showed no response to nitrogen fertilization. Recent study on environmental and economic benefit analysis of Napier grass has been reported by Tsai and Tsai (2016). Their result shows that Napier grass can mitigate CO_2 emissions to the order of 5 million Gg per annum. The energy equivalent was found to be 11 million barrels per 100 000 hectare annually which equals to 110 barrels of oil energy equivalent per hectare. This value strongly agrees with the findings reported by Samson et al. (2005) and Flores et al. (2012). Cultivation of Napier grass follows conventional farming practices. It outcompetes weeds and therefore, requires lower establishment costs. This makes it one of the best potential energy crops for the development of efficient and economic bioenergy systems (Samson et al., 2005; Flores et al., 2012). Recently, investigations have also shown that Napier grass can be incorporated into tree plantations such as oil palm, rubber tree plantations where there are large areas of unused spaces, estimated at 26.63% of the total space (Zhou et al., 2012; Mohammed et al., 2015a). Mohammed et al. (2015a) reported that intercropping Napier grass with oil palm produce thick elongated Napier grass stem, which contained more biomass than the Napier grass grown under unshaded conditions. This therefore offers another economic benefit.

Pyrolysis is the thermal decomposition of biomass in total absence of oxygen to produce solid, liquid and gas products. This process has high improved efficiency, environmental suitability and flexibility as virtually any biomass type can be handled to generate various products (Heidenreich and Foscolo, 2015; Mohammed et al., 2016c). In addition, high liquid yield (known as bio-oil) which is of most interest can be obtained through pyrolysis process under a careful control of process variables such as inert gas flowrate, pyrolysis temperature, heating rate, vapor residence time, reactor type, and the temperature regime between the reaction and cooling zone (Bridgwater, 2012; Eom et al., 2012). Generally, pyrolysis process is classified into slow, intermediate and fast pyrolysis. In slow pyrolysis (carbonization), temperature up to 400 °C, vapor residence time of 60 minutes to days are used and a typical product yield of about 35 % bio-char, 30 % bio-oil, and 35 % non-condensable gas. For fast pyrolysis, temperature of about 500 °C, high heating rate (up 1000 ^{o}C/min) and short vapor residence time of approximately 1 s are applied. Nearly 80 % bio-oil yield (wet basis), and about 13 and 12 % non-condensable gas and bio-char are obtained. (Bridgwater, 2012; Mohammed et al., 2015b). On the other hand, intermediate pyrolysis produces about 40-60 % bio-oil, 15-25 % bio-char and 20-30 % non-condensable gas under process condition of 500-650 ^{o}C and 10 to 30 s vapor residence time. Intermediate pyrolysis has added advantages over the fast pyrolysis in that the oil from it is less reactive and may be used directly as fuel in engines and boilers. It also produces dehydrated char, which can be used for both agricultural and energy applications (Tripathi et al., 2016; Mohammed et al., 2016c). However, production of bio-oil from biomass via pyrolysis requires energy at different stages. Energy is consumed during biomass collection, bio-oil production stage (size reduction, feeding, pyrolysis and cooling) and bio-oil transportation. Study has shown that about 82 % of the total energy requirement for a bio-oil production process is consumed at the production stage mainly during size reduction and pyrolysis (high temperature is needed to decompose the biomass) (Ning et al., 2013). Though, the challenge of high energy requirement may be compensated through efficient utilization of other pyrolysis products (bio-char and non-condensable gas). Climate change mitigation is an unresolved issue between the cons and pros of biofuels utilization. Production of biofuel can be said to reduce greenhouse gases only when it produce residuals that render the use of fossil fuels unnecessary. Consequently, production of second generation biofuels should be carefully synchronized to encourage more agricultural food production and the use of marginal lands for cultivation of energy crops in order to develop a sustainable bioenergy system (Caputo, 2014).

Utilization of Napier grass for the development of biofuels via pyrolysis is very limited. Strezov et al. (2008) reported thermochemical conversion of Napier grass to bio-oil, bio-char and non-condensable gas using a pyro-probe type reactor. They investigated effect of heating rate (10 and 50 ^{o}C/min) on the pyrolysis product distribution. In each case, the system was ramped to a maximum temperature of 900 ^{o}C. Their result showed that the bio-oil collected was made up of organic acids, phthalate esters, and larger fraction of various benzene chemicals, phenols and pyrans. They reported that the high heating rate of 50 ^{o}C/min promoted the formation of smaller acids and benzene fractions in the bio-oil compared to the low heating rate of 10 ^{o}C/min. CO_2 was found to be the major component in the non-condensable gas. They stated that the bio-oil collected was a two-phase liquid and sample was analyzed with GC-MS without separation into individual phases. Although, a mixture of methanol and chloroform was used as solvent but there is high tendency of phase separation during the GC-MS analysis and the sample injected may not be the true representation of the whole bio-oil. Lee et al. (2010) reported pyrolysis of Napier grass in an induction-heating reactor. They investigated effect of heating rate between 50 and 200 ^{o}C/min and biomass particle size within 2 mm at pyrolysis temperature of 500 ^{o}C. Their findings also showed that bio-oil yield increased with heating rate from 50 to 150 ^{o}C/min but declined thereafter. Maximum bio-oil yield of 36 wt% was reported at 150 ^{o}C/min with 0.224 mm biomass particle size. The bio-oil yield was lower than those generally obtained from a fast pyrolysis system (50-60 wt%) and was attributed to the low level of heating rate used compared to the fast pyrolysis where up to 1000 ^{o}C/min is normally employed. This conclusion may not be valid as the study was conducted under a constant temperature of 500 ^{o}C, which may not be the optimum temperature for complete devolatilization of various structural components in the biomass. Pyrolysis product distribution is strongly related to the pyrolysis temperature and vapor residence time in the reactor compared to the heating rate (Bridgwater, 2012; Mohammed et al., 2015b). Their findings also reveal that the bio-oil was predominantly acetic acid, phenols, ketones, and nitrogenated hydrocarbons. These chemical species are polar compounds that are generally present in the aqueous phase of the bio-oil. The major composition of the non-condensed gas reported were furans, olefins and mono-aromatic hydrocarbons (benzene, toluene and xylene), which are normal component of the condensate. This means that the cooling system used during the study was inefficient. Thus, the composition of the bio-oil reported does not represent the whole condensables from the Napier grass.

A study recently conducted by Sousa et al. (2016) on pyrolysis of Napier grass in a fluidized bed reactor with a feed rate between 20 and 35 kg/h, temperature at around 500 ^{o}C. Maximum oil yield of 28.2 % was recorded. This yield was also far lower relative to a typical bio-oil yield (40-60 %) from a fluidized bed pyrolysis system. The authors attributed it to the accumulation of heavier fractions within the system before the cooling zone. The bio-oil composition reported had principally phenolics, organic acids and traces of levoglucosan and mono-aromatic hydrocarbons. H_2, CO, CO_2, CH_4 and C_2H_6 were the main component detected in the non-condensable gas. However, the yield and composition of the bio-oil collected may have been affected as the authors stated that air was employed as the fluidizing gas instead of an inert gas. Effect of other temperature levels and variations in the fluidizing gas velocity were not investigated. Similarly, De Conto et al. (2016) studied pyrolysis of Napier grass in a rotary kiln reactor where the effect of pyrolysis temperature and rotating speed of the reactor were investigated. Information regarding the bio-oil collected by the authors was only limited to the yield. Physicochemical properties and chemical compositions of the bio-oil were not determined. The non-condensable gas analyzed particularly at 600 ^{o}C was made up of high hydrogen (H_2)/carbon monoxide (CO) ratio which was attributed to the temperature only. However, this may be a combined effect of temperature and vapor residence time in the reactor. From the reactor size and carrier gas flowrate reported by the authors, vapor residence was around 1.425 min (85 sec), which is long enough to result to severe secondary cracking of the pyrolysis vapor at such a high temperature. Some classical studies on the pyrolysis of Napier grass have also been reported by our research group recently (Mohammed et al., 2015b; Lim et al., 2015, Mohammed et al., 2016a, 2016b, 2016d, Lim et al., 2016). To date, no study on pyrolysis of Napier grass is available in the literature that deals with collective examination of pyrolysis temperature, heating rate, inert gas flowrate on the products distribution and composition. This investigation is needed in order to appropriately evaluate the energy potential of the biomass.

The objective of this study was to evaluate collective effects of heating rate, pyrolysis temperature and nitrogen flow rate on the pyrolysis products distribution and optimize bio-oil yield from intermediate pyrolysis of Napier grass using response surface methodology (RSM) based on a central composite design (CCD).

2. Materials and Methods

2.1 Material and characterization

Fresh locally grown Napier grass stem (NGS) was collected from the Crops for the Future (CFF) Field Research Centre. The material was oven dried at 105 °C for moisture content determination and thereafter shredded in a Retsch® rotor beater mill. The ground biomass sample (0.2 -2.5 mm) was collected and preserved in airtight plastic bags for further analysis. Proximate and ultimate analyses on dry basis were carried out according to the relevant standard procedures. Major inorganic elements in the ash were determined using atomic absorption spectrometer (AAS) Perkin Elmer analyst 400 (Perkin Elmer Sdn Bhd, Selangor, Malaysia). Higher heating value (HHV) was determined using a Parr 6100 oxygen bomb calorimeter. Elemental compositions were determined using a Perkin Elmer 2400 Series II CHNS/O analyzer (Perkin Elmer Sdn Bhd, Selangor, Malaysia). The structural analysis of the biomass was performed using High-performance liquid chromatography (HPLC-1260 infinity, Agilent Technologies Sdn Bhd, Selangor, Malaysia). Thermogravimetric analysis was conducted with the thermal analyzer (STA) 6000 (TGA) (Perkin Elmer Sdn Bhd, Selangor, Malaysia) in a nitrogen atmosphere, flow rate 20 mL/min at temperatures between 30-950 ^{o}C and heating rate of 10 ^{o}C/min. About 10.0 mg (particle size of 0.2 mm) of sample was used.

2.2 Pyrolysis experiment

Intermediate pyrolysis study was carried in a vertical tube fixed bed pyrolysis system as shown in Figure 1. The system consists of a fixed bed reactor made of stainless steel (115 cm long, 6 cm inner diameter), a distribution plate with 1.5 mm hole diameter which sits at 25 cm from the bottom of the tube, two nitrogen preheating sections, a cyclone, water chiller operating at 3 ^{o}C attached to a coil condenser, oil collector and gas scrubbers. 200 g of NGS (bone dry, 2.5 mm particle size) was placed on the distribution plate inside the reactor tube and pyrolysis was conducted under nitrogen atmosphere. The reaction temperature was monitored with a K-type thermocouple connected to a computer through data logger. The reaction time was kept at 60 min after the temperature reaches the desired value. The pyrolysis vapor was condensed by passing through a condenser connected to a chiller at 3 ^{o}C and the oil was collected. The bio-oil, bio-char and non-condensable gas yield was computed according to equation (1), (2) and (3) respectively. 20 sets of pyrolysis experiments were conducted based on the number generated by the statistical software where the pyrolysis temperature (450-750 ^{o}C), nitrogen flow rate (5-25 L/min) and heating rate (10-50 ^{o}C/min) were selected in this study.

$$\text{Yield}\left[\text{wt\%}\right]_{\text{bio - oil}} = \left[\frac{\text{weight of the bio - oil collected}}{\text{weight of biomass feed}} \times 100\right] \text{- - - - - - - -} (1)$$

$$\text{Yield}\left[\text{wt\%}\right]_{\text{bio - char}} = \left[\frac{\text{weight of the bio - char collected}}{\text{weight of biomass feed}} \times 100\right] \text{- - - - - -} (2)$$

$$\text{Yield}\left[\text{wt\%}\right]_{\text{non - condensable gas}} = 100 - \left(\text{Yield }[\text{wt\%}]_{\text{bio - oil}} + \text{Yield }[\text{wt\%}]_{\text{bio - char}}\right) \text{- - - -} \quad (3)$$

Figure 1: Experimental set-up. (1) Nitrogen cylinder, (2) nitrogen preheating sections, (3) pyrolysis section, (4) furnace controller, (5) heater, (6) insulator, (7) thermocouples, (8) data logger, (9) computer, (10) water chiller, (11) cyclone, (12) condenser, (13) bio-oil collector, (14) gas scrubber, (15) gas sampling bag, (16) gas venting

2.3 Response surface methodology (RSM)

The response surface methodology (RSM) is a statistical and mathematical technique for designing experiments to provide reliable measurements of the desired response which may be affected by many variables. A mathematical model with the best fit is usually developed using data from the experimental design and the optimal value of the variables that produces maximum or minimum response are determined. In this study, RSM was used following the face central composite design (FCCD) method with the aid of Design expert software (Version 6.0.6, Stat-Ease Inc., MN, USA). The CCD consists of 8 cube (factorial) points, 6 axial points and 6 replicates at centre points which translate to a number of experiments and 20 experiments were generated according to equation (4). The variables and the experimental domain in this design are presented in Table 1. At the end of the experiment, the results were fitted to second-degree polynomial design as shown in the equation (5) below.

$$\mathrm{N} = 2^{\mathrm{n}} + 2n + n_{c} = 2^{3} + 2\times 3 + 6 = 20 ---------- (4)$$

Where N is the number of experiments, n is the number of factors and n_c is the number of replicates at the centre point.

$$\mathrm{Y} = \beta_{\mathrm{o}} + \sum_{\mathrm{i=1}}^{\mathrm{n}} \beta_{\mathrm{i}} \mathrm{X}_{\mathrm{i}} + \sum_{\mathrm{i=1}}^{\mathrm{n}} \beta_{\mathrm{ii}} \mathrm{X}_{\mathrm{i}}^{2} + \sum_{\mathrm{i=1}}^{\mathrm{n}} \sum_{\mathrm{j>1}}^{\mathrm{n}} \beta_{\mathrm{ij}} \mathrm{X}_{\mathrm{i}} \mathrm{X}_{\mathrm{j}} ---------- (5)$$

Where Y is the predicted response, n is the number of experiments, β_o, β_i, β_{ii} and β_{ij} is regression coefficients for the constant, linear, quadratic and interaction terms, respectively. X_i and X_j are the coded independent factors. The adequacy of the final model was tested using both graphical and numerical analysis and the experimental data were analysed statistically using analysis of variance (ANOVA).

Table 1: Range of independent variables and experimental levels

2.4 Pyrolysis products characterizations

Pyrolysis oil collected at optimized condition was further analyzed. Physicochemical properties of the bio-oil such as pH, water content, calorific value, density and viscosity were analyzed with a WalkLAB microcomputer pH meter (TI9000, Trans Instruments, Singapore), Karl Fischer V20 volumetric titrator (Mettler Toledo, Columbus, OH, USA), oxygen bomb calorimeter (Parr 6100, Parr Instruments, Molin, IL, USA), Anton Paar density meter (DMA 4500 M, Ashland, VA, USA) and Brookfield viscometer (DV-E, Hamilton, NJ, USA) respectively. Carbon, hydrogen, nitrogen, sulfur and oxygen contents of the bio-oil were determined with a CHNS/O Analyzer (2400 Series II CHNS/O analyzer, Perkin Elmer Sdn Bhd, Selangor, Malaysia). Functional group analysis was performed with fourier transform infrared-FTIR (Spectrum RXI, PerkinElmer, Selangor, Malaysia) using a pair of circular demountable potassium bromide (KBr) cell windows (25mm diameter and 4mm thickness). Spectra were recorded with Spectrum V5.3.1 software within wave number range of 400-4000 cm^{-1} at 32 scans and a resolution of 4 cm^{-1}. Fractionation of the organic phase bio-oil was simulated using TGA in nitrogen atmosphere at 20mL/min, 10^oC/min from ambient to 500^oC to examine the volatile fractions and the result was compared with the simulated distillation of fossil-gasoline, kerosene and diesel. Detail of the chemical composition of the bio-oil was determined using a gas chromatograph-mass spectrometer (GC-MS) (PerkinElmer Clarus® SQ 8, Akron, OH, USA) with a quadruple detector and column (30m x 0.25mm x 0.25µm) (PerkinElmer-Elite^{TM}-5ms, Akron, OH, USA). The oven was programmed at an initial temperature of 40 °C, ramp at 5 °C /min to 280 °C and held there for 20 min. The injection temperature, volume, and split ratio were 250 °C, 1 µl, and 50:1 respectively. Helium was used as carrier gas at a flow rate of 1 mL/min. The peaks of the chromatogram were identified by comparing with standard spectra of compounds in the National Institute of Standards and Technology library (NIST, Gaithersburg, MD, USA).

Samples of the non-condensable gas were collected in SKC polypropylene fitted gas sampling bag and analyzed offline with a gas chromatography (PerkinElmer Clarus 500, Akron, OH, USA) equipped with stainless steel column (Porapak R 80/100) and thermal conductivity detector (TCD). Helium was used as a carrier gas and the GC was programed at 60 ^{o}C, 80 ^{o}C and 200 ^{o}C for oven, injector and TCD temperature respectively. Bio-char proximate and ultimate analyses were performed following the same analytical procedure adopted for the feedstock characterization above. Scanning electron microscopy (SEM, FEI Quanta 400 FE-SEM, Hillsboro, OR, USA) and physisorption analyzer (ASAP 2020 Micrometrics, Norcross, GA, USA) were used to evaluate the surface and structural characteristics, and specific surface area (BET) and pore properties of the bio-char respectively.

3. Results and Discussion

3.1 Feed stock characteristics

Characteristic of NGS used in this study is summarized in Table 2. The proximate analysis result obtained showed significant difference relative to similar properties of Napier grass (NG) reported in the literature. Higher volatile matter and lower ash contents were recorded compared to the values reported by Strezov et al. (2008), Lee et al. (2010), Braga et al. (2014) and De Conto et al. (2016). Higher heating value (HHV) was 18.05 MJ/kg relative to 15.61 MJ/kg and 15.77 MJ/kg reported by Braga et al. (2014) and De Conto et al. (2016) respectively. These variations in the proximate analysis result is attributed to the post-harvest treatment of the NG sample used. The results of ultimate and structural analyses (Table 2) showed good agreement with the literature values. Comparing the structural characteristics of NGS with that of switchgrass and miscanthus, from the work of Imam and Capareda (2012) and Rena et al. (2016), switchgrass has lower cellulose (32-34 wt%) and lignin (18.8 wt%) contents. Similarly, miscanthus has lower lignin content (12-12.58 wt%) but higher cellulose (50.34-52.13 wt%) and hemicellulose (24.83-25.76 wt%) contents as reported by Brosse et al. (2012) and Shemfe et al. (2016). Studies on the detail mineral composition of NG biomass is rarely reported. This characteristic is very important for biomass thermochemical conversion. For pyrolysis, it has been reported that mineral composition of biomass has great influence on both product yield and bio-oil composition (Mohammed et al., 2016b). Most researchers employed x-ray fluorescence (XRF), energy dispersive x-ray (EDX) in determining the mineral composition of biomass. These techniques provide elemental composition at a specific point within the sample instead of the mineral distribution in the whole sample. Strezov et al. (2008) reported silicon (Si), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), aluminum (Al) and sodium (Na) using XRF as the major elements present in the Napier grass biomass. In this study, the major elements recorded in the feedstock using atomic absorption spectrometer (AAS) showed similar mineralogical composition (Na, K, Ca, Al, Fe and Si).

Table 2: Characteristics of Napier grass biomass used

The thermogravimetric profile of NGS is presented in Figure 2. The sample was heated in nitrogen atmosphere (20 mL/min) at 10 ^{o}C/min from ambient temperature to 100 ^{o}C and held there for 30min to eliminate all the physically absorbed moisture and thereafter, ramped to 900

^{o}C. Pyrolysis of a lignocellulosic biomass proceeds through simultaneous decomposition of hemicellulose, cellulose and lignin of the biomass with each component displaying separate mechanism, which makes the process so complex (Kan et al., 2016; Anca-Couce, 2016). Most studies have focused on the classical evaluation of degradation of the individual components as a foundation of the likely decomposition pathway. However, research have shown that there is interaction between the structural components of the biomass during pyrolysis, which is also affected by the mineral content of the biomass (Kan et al., 2016; Anca-Couce, 2016). In this study, pyrolysis profile of NGS from the TG/DTG showed four distinct regions at temperature around 200 ^{o}C, 229-285 ^{o}C, 326 ^{o}C and 373-540 ^{o}C. Visible peak at about 200 ^{o}C was observed, which is due to the decomposition of extractives. This could also be due further dehydration of the biomass through cleavage of hydroxyl groups in the hemicellulose, cellulose and lignin (Van de Velden et al., 2010; Collard and Blin, 2014). The total weight loss recorded under this region was 12.58 wt%. A shoulder is observed at temperature between 229 and 285 ^{o}C and is ascribed to the fast decomposition of hemicellulose as a result of cleavage of the glyosidic bond between the monomeric units. Depolymerization of cellulose to active cellulose is also expected within this temperature range (Van de Velden et al., 2010; Collard and Blin, 2014). The corresponding weight loss of 13.66 wt% was recorded. The main characteristic peak was observed at 326 ^{o}C. This is attributed to cellulose decomposition and had a maximum weight loss of 35.74 wt%. Temperature between 373 and 540 ^{o}C represent degradation of lignin due to carbon-carbon scission and disruption of aromatic rings within the lignin structure, which resulted in weight loss of 10.78 wt%. Temperature beyond 540 ^{o}C represent transformation of the remaining solid (char) through aromatization and demethylation (Patwardhan et al., 2011; Collard and Blin, 2014). Similar decomposition profile of NG has also been reported by Braga et al. (2014). They ascribed peaks observed at temperature range of 180-300 ^{o}C, 300-380 ^{o}C and 380-530 ^{o}C to the decomposition of hemicellulose, cellulose and lignin respectively. Similarly, De Conto et al. (2016) studied thermogravimetrics of NG and reported decomposition of cellulose at 318 ^{o}C and lignin with 350-500 ^{o}C. These decomposition temperature ranges has also been reported in the literature for other lignocellulosic biomass (Gómez et al., 2016)

Figure 2: Thermogravimetric profile of Napier grass stem (TG and DTG)

3.2 Central composite design (CCD) and statistical analysis

Experiments were conducted according to the experimental designed matrix and the responses (bio-oil, bio-char and non-condensable gas yields) are presented in Table 3. The experimental results were fitted to second-degree polynomial model as shown in the (6), (7) and (8) below. Where A, B and C is the temperature (^{o}C), nitrogen flow rate (L/min) and heating rate (^{o}C/min). Analysis of variance (ANOVA) for each response model was carried to establish its significance and nature of interactions between the process variables (Table 4a-c).

$$Y_{bio-oil} = 49.37 + 2.03A - 0.70B + 2.04C - 13.31A^2 + 0.75B^2 - 0.83C^2 - 0.67AB - 1.88AC + 0.09BC \text{-------} (6)$$

$$Y_{bio-char} = 21.78 - 11.89.A + 0.66B - 0.73C + 10.32A^2 - 0.14B^2 - 0.72C^2 - 0.61AB + 0.27AC - 0.52BC \text{-------} (7)$$

$$Y_{Non-condensable-gas} = 28.85 + 9.85.A + 0.04B - 1.31C + 2.99A^2 - 0.61B^2 + 1.55C^2 + 1.28AB + 1.61AC + 0.43BC \text{---} (8)$$

Table 3: CCD Experimental Design Matrix and Response

For the bio-oil yield, the Model F-value of 171.60 (Table 4a) implies the model is significant. Lack of Fit F-value of 3.18 implies that it is not significant relative to the pure error. Nonsignificant lack of fit is desirable because it is wanted to fit. For the bio-char and non-condensable gas yield, similar trends are observed. Model F-value of 151.22 (Table 4b) and 69.74 (Table 4c) with the corresponding lack of fit F-value of 1.47 and 3.41 are recorded. Values of "Prob > F" less than 0.0500 indicates model terms are significant while values greater than 0.1000 indicate the model terms are not significant.

In the case of bio-oil, the significant model terms are A, B, C, A^2, AB, AC, with the corresponding F-value of 62.92, 7.46, 63.59, 741.20, 5.52, and 43.12. It can also be observed that the most significant model term on the bio-oil yield obeyed the following order $A^2>A>C>AC>B>AB$ while the quadratic terms B^2, C^2 and the interaction BC does not have a significant impact on the bio-oil yield. For bio-char, the significant model terms are A and A^2 with the linear term having the largest significance due higher F-value of 1006.27 (Table 4b). The significant model terms for the non-condensable gas are A, C, A^2, AB, AC, with A being the most significant term having F-value of 557.41 (Table 4c). The coefficient of determination, R^2 for the bio-oil, bio-char and non-condensable gas model is 0.9936, 0.9927 and 0.9843 respectively (Table 4a-c). Another regression parameter considered is the adjusted R2, which improves the coefficient of determination (R^2) in relation to the sample size and the model terms, and the corresponding value is 0.9878, 0.9861 and 0.8903. The R^2 and adjusted R^2 values for the individual model are high enough and comparable, which indicate that the selected quadratic response surface model for the pyrolysis products sufficiently describe the experimental data within the selected operating conditions. Also, the predicted R^2 value of the bio-oil, bio-char and the non-condensable gas model is 0.9518, 0.9411 and 0.8903 respectively which is in good agreement with the respective adjusted R^2 values. Adequate precision (Adeq Precision) is a measure of signal to noise ratio and a ratio greater than 4 is desirable. In this study, the value of Adeq precision is 36.4925, 32.8072 and 27.3167 for the bio-oil, bio-char and non-condensable gas model respectively. These high values indicate adequate signal and the models can be used to navigate the design space. Furthermore, the coefficient of variation (CV) which is a measure of the reliability of the experiment, it expresses the overall experimental error as a percentage of the overall mean. The CV value recorded for the pyrolysis products is less than 4.5, hence, this experiment can be said to be highly reliable since the lower the CV value, the higher is the reliability of the experiment.

Table 4: ANOVA test for **(a)** bio-oil, **(b)** bio-char, **(c)** non-condensable gas response model and respective model term

3.3 Model validation and response surface plot

To further evaluate the adequacy of the quadratic models in fitting the experimental data, diagnostic plots (normal % probability against studentized and outlier T against a number of runs) were established and are presented in Figure 3 (a and b). In the Figure 3a, the points are distributed approximately on a straight line along the diagonal for each of the pyrolysis product models. This trend depicts that the error terms are normally distributed and independent of each. Furthermore, from Figure 3b, the points are randomly distributed around zero on the outlier T axis and between +3.5 and -3.5 in all the cases, which connote homoscedasticity and therefore suggest that the respective model is suitable and successfully establish the relationship between the pyrolysis process variables studied and the product distribution.

Figure 3: Diagnostics of models (a) Normal % probability versus studentized residuals (b) Outliers T versus run number

In order to examine the effect of the pyrolysis process variables on the response values, interaction and 3D surface plots were used. Although, it is not possible to present the effects of all the parameters studied on the same 3D, as such, the response surface plots are presented by varying two factors and keeping one factor constant as shown in Figure 4(a-f), 5(a-f) and 6(a-f) for bio-oil, bio-char and non-condensable gas yields respectively. The interaction between the nitrogen flow and temperature at a constant heating rate (30 ^{o}C/min) on the bio-oil yield (Figure 4a-b) shows that increase in the nitrogen flow rate from 5 L/min to 25 L/min and temperature from 450^{o}C to 600 ^{o}C increased the bio-oil yield. The oil yield became maximum at 600 ^{o}C for both nitrogen levels but at a different amount. Lower nitrogen level (5 L/min) produced 52.06 wt% oil compared to 49.20 wt% oil yield at 25 L/min nitrogen flow at the same 600 ^{o}C. The decreased oil yield at the higher nitrogen flow rate could be as a result of more uncondensed volatiles leaving as part of non-condensable gas due to short vapor residence time in the condenser. Declines in the oil yields were observed at temperature above 600 ^{o}C. The bio-oil yield trend recorded with temperature from 450 ^{o}C to 600 ^{o}C and above 600 ^{o}C can be respectively ascribed to degradation of more lignin, and secondary reactions of pyrolysis vapor and more decomposition of bio-char at the elevated temperature (Soetardji et al., 2014). The effect of heating rate and temperature on the bio-oil yield at a constant nitrogen flow rate (15 L/min) is presented in Figure 4c-d. Increasing temperature from 450 to 600 ^{o}C and heating rate between 10 and 50 ^{o}C/min increased the oil yield from 29.26 to 46.13 wt% and 37.12 to 50.89 wt% respectively. The yield of more bio-oil at 50 ^{o}C/min relative to 10 ^{o}C/min under the same pyrolysis temperature is attributed to rapid depolymerization of the biomass to primary volatiles at the higher heating rate. (Yorgun and Yildz, 2015). The oil yield decreased to 37.10 wt% at both heating rates under the same temperature (750 ^{o}C) and nitrogen flow (15 L/min) due to secondary reactions at such a high temperature. The combined effects of heating rate and nitrogen flow rate at a pyrolysis temperature of 600 ^{o}C on the bio-oil yield is shown in Figure 4e-f. As the nitrogen flow increased from 5 L/min to 25 L/min, bio-oil yield at 50 ^{o}C/min heating rate remained higher compared to the oil collected at 10 ^{o}C/min but no significant impact of nitrogen flow was observed in both cases. Bio-oil yield at 50 ^{o}C/min was between 50.72 and 51.94 wt% relative to 46.45-48.03 wt% oil recorded at 10 ^{o}C/min.

Figure 4: Interaction graphs and the corresponding surface response plots for the combined effects of process variables on bio-oil yield. (a) and (b) effect of nitrogen flow and temperature at 30^{o}C/min; (c) and (d) effect of heating rate and temperature at 15L/min N_2; (e) and (f) effect heating rate and nitrogen flow at 600^{o}C

Impacts of pyrolysis temperature, heating rate and nitrogen flow rate on the yield of bio-char are shown in Figure 5 (a-f). Interactions between temperature and nitrogen flow Figure 5 (a-b) showed that the temperature had great influence on the bio-char yield compared to the nitrogen flow rate. A general decline in the bio-char yield was recorded with increasing temperature at both 5 L/min and 25 L/min nitrogen flow rates, which is attributed to devolatilization more organic materials as dehydration of hydroxyl groups and decomposition of lignocellulose structure progresses with increasing temperature (Mohammed et al., 2015b). This clearly demonstrated that bio-char yield is governed by the pyrolysis temperature. The impact of temperature also dominated interaction between temperature and heating rates on the bio-char yield (Figure 5c-d). There was no considerable difference between the bio-char yields at 10 ^{o}C/min and 50 ^{o}C/min throughout the investigated temperature range. Bio-char yields recorded were 44.27 wt% and 42.27 wt% at 450 ^{o}C, and 20.59 wt% and 19.03 wt% at 750 ^{o}C for 10 ^{o}C/min and 50 ^{o}C/min heating rate respectively. The slightly lower value of bio-char recorded at 50 ^{o}C/min could also be attributed to rapid degradation of biomass. Influence of heating rate and nitrogen flow on the bio-char yield is presented in Figure 5(e-f). Both factors did not significantly impacted on the char yield. As nitrogen flow increased from 5 L/min to 25 L/min, bio-char yield at 50 ^{o}C/min remained the same (around 20 wt %) while between 20.48 to 22.84 wt% char yield was recorded at 10 ^{o}C/min under the same nitrogen flow regime. These observations indicated that the range of nitrogen flow rates used in this study was sufficient in preventing secondary reaction such as condensation which normally favored char formation (Yorgun and Yildz, 2015).

Figure 5: Interaction graphs and the corresponding surface response plots for the combined effects of process variables on bio-char yield. (a) and (b) effect of nitrogen flow and temperature at 30^{o}C/min; (c) and (d) effect of heating rate and temperature at 15L/min N_2; (e) and (f) effect heating rate and nitrogen flow at 600^{o}C

Effects of process variables on the production of non-condensable gas are shown in Figure 6 (a-f). The interaction between temperature and nitrogen flow (Figure 6a-b) revealed that non-condensable gas yield increased with temperature at both nitrogen flow levels. As the temperature progressed from 450 to 600 ^{o}C, the increase in the gas yield was not significant under 5 L/min nitrogen flow. This indicates the most of the volatiles generated during the pyrolysis are effectively captured in the condenser, which eventually ended up in the bio-oil as rightly identified in the bio-oil yield section above. The significant change in the gas yield recorded under 25 L/min nitrogen flow between 450 and 600 ^{o}C is mainly due to shorter vapor residence time in the condenser compared to the 5 L/min nitrogen flow rate. With increasing temperature above 600 °C, the gas yield increased rapidly in both nitrogen flow regimes, which can be ascribed to further thermal decomposition of pyrolysis vapor in addition to some uncondensed volatiles leaving the pyrolysis system as part of non-condensable gas, particularly at the higher flow rate. 30.21-42.40 wt% gas yield was recorded with 25 L/min nitrogen flow relative to 26.05-39.77 wt% gas yield using 5 L/min. Furthermore, the combined effects of temperature and heating rate on the yield of non-condensable gas (Figure 6c-d) also revealed that the temperature has great influence on the gas yield. With increasing temperature from 450-750 °C, the non-condensable gas yield increased from 26.46 to 42.94 wt% and 20.62 to 43.55 wt% at 10 °C/min and 50 °C/min respectively. This trend is believed to be as a result of secondary cracking of volatiles and further decomposition of bio-char at higher temperatures (Yorgun and Yildz, 2015). On the other hand, nitrogen flow and the heating rate seem to have no considerable impact on the yield of non-condensable gas (Figure 6e-f). As the nitrogen flow rate increased from 5L/min to 25L/min, the change in the yield of non-condensable gas was insignificant at both 10°C/min and 50°C/min. Gas yield of 28.02-28.95 wt% and 30.71-31.50 wt% were recorded with 10 and 50°C/min heating rate respectively throughout the carrier gas flow range used in this study.

Figure 6: Interaction graphs and the corresponding surface response plots for the combined effects of process variables on non-condensable gas yield (a) and (b) effect of nitrogen flow and temperature at 30°C/min; (c) and (d) effect of heating rate and temperature at 15L/min N_2; (e) and (f) effect heating rate and nitrogen flow at 600°C

3.4 Optimization and validation of result

In order to maximize the bio-oil yield, the process variables considered in this study were optimized. Pyrolysis temperature, heating rate, and nitrogen flow rate were maintained within the range of experimental condition studied while the bio-char and non-condensable gas responses were minimized (Table 5a). Based on these conditions, eight (8) solutions were generated by the software as presented in Table 5(b). Solution number one (1) with the highest desirability was chosen. This indicates that the pyrolysis temperature of around 600 ^{o}C, 5 L/min nitrogen flow rate, and 50 ^{o}C/min heating rate was sufficient to produce optimum bio-oil of 51.94 wt%. This result was validated by performing further experiments under the optimized process condition. The experiment was repeated in triplicates and the results are shown in Table 6. The average value of bio-oil yield recorded (50.57 wt%) sufficiently agree with the predicted value. Consequently, this validation confirms the adequacy of the developed quadric model for bio-oil yield.

Table 5: (a) Optimization condition (constraints) **(b)**: Optimized solutions

Table 6: Bio-oil yield predicated at the optimized condition and experimental value

The bio-oil yield from NGS observed at the optimized condition (600 ^{o}C, 5 L/min N_2 and 50 ^{o}C/min) in this study is similar to the liquid product reported by Strezov et al. (2008) during the pyrolysis of NG. They observed 54.37 wt% bio-oil yield at 50 ^{o}C/min and 500 ^{o}C pyrolysis temperature under argon atmosphere. Similarly, the result of pyrolysis study of NG by De Conto et al. (2016) showed a total bio-oil yield of 52.99 wt% at 700 ^{o}C, 25 ^{o}C/min and 1 L/min nitrogen flow. Sousa et al. (2016) also reported a total liquid product of 48.2 wt% from the pyrolysis of NGS at 540^{o}C. Report by Lee et al. (2010) on NG pyrolysis showed a lower oil yield of 36 wt% at 500 ^{o}C and 150 ^{o}C/min higher heating rate under nitrogen atmosphere. These variations in the yield of bio-oil from NG biomass can be linked to the characteristic of the feedstock used, heating and heat transfer rates of the reactor, and the difference in the pyrolysis condition (temperature, inert gas flow).

3.5 Physicochemical properties of bio-oil produced at optimized condition

The bio-oil product collected throughout this study was two-phase liquid, the organic phase (high molecular weight component) and aqueous phase (low molecular weight component). The organic fractions are usually water-insoluble derived from lignin component of the feed biomass while the light fractions consist predominantly water (originates from both moisture in the feed biomass and pyrolysis reaction), acids, ketones, aldehydes, small fraction of phenols and other water-soluble organics (Resende et al., 2015). The physicochemical characteristics of the oil produced at optimized condition are summarized in Table 7. Both the organic and aqueous phases present an acidic characteristics with corresponding pH values of 3.71 and 2.09. This property is attributed to presence of organic acids and phenolics in the bio-oil. The presence of water in the pyrolysis oil is mainly from moisture in the feed biomass and product of dehydration during the pyrolysis reaction (Resende et al., 2015; Mohammed et al., 2015b). In this study, the biomass feedstock used was bone dry and, therefore, the water content of the oil could be said to have originated from the pyrolysis reaction. Despite a careful separation of the aqueous phase, 7.24 wt% water remained in the organic phase. Solid content of the organic phase was determined as ethanol insoluble. Bio-oil concentration of 1.25 wt% (1 g of bio-oil sample in 80 g of ethanol) was used. The mixture was agitated and then filtered using 0.1µm filter. The filter and retentates was thereafter oven dried at 105 ^oC for 30 min. Total solid content of less than 0.01 wt% (0.008-0.009) was recorded. Other characteristics of the organic phase such as density, viscosity, ash content and calorific value reasonably conform to the ASTM specifications for pyrolysis oil. Consequently, the organic phase bio-oil from NGS can be regarded as ASTM-Grade D bio-oil. Carbon and oxygen contents from the ultimate analysis revealed that the organic phase bio-oil has higher carbon (51.14 wt%) and lower oxygen (41.66 wt%) compared to the value reported by Lee et al. (2010) (6.04 wt%-carbon); Sousa et al. (2016) (41.85 wt%-carbon). High carbon content in the organic phase connotes presence carbon-rich organic molecules which have resulted in the higher heating value (HHV) of 26.42 MJ/kg.

Table 7: Physicochemical properties of bio-oil produced at the optimized condition

3.6 *Fourier-transform infra-red (FTIR)*

FTIR spectra of chemical species in the bio-oil samples are shown in Figure 7 (a & b). The common broad peak around 3439 cm^{-1} implies that the samples contain chemical compounds with hydroxyl group ($O-H$) such as water, alcohols and phenol (Guo et al., 2015; Bordoloi et al., 2015). The peak at a frequency around 2970 cm^{-1} is due $C-H$ stretching vibration which is present only in the Figure 6b indicating the presence of saturated hydrocarbon in the organic phase while the peak at a frequency around 2100 cm^{-1} common to both phases is ascribed to the $C \equiv C$ functional group (Guo et al., 2015; Bordoloi et al., 2015). Vibration observed between 1625 cm^{-1} and 1707 cm^{-1} in both oil phases is attributed to $C = O$ which signifies the presence of aldehydes, ketones or carboxylic acids. The vibration around 1462 cm^{-1} present in the organic phase is ascribed $C = H$ indicating the presence of alkenes/aromatic hydrocarbons while the peak between 1388 and 1364 cm^{-1} in both cases is due to $C-H$ bond (Yorgun and Yildz, 2015). The sharp band around 1221, 1269, 1016 and 1092 cm^{-1} are due to $C-O$ vibration indicating the presence of alcohol and esters. The fingerprint between 900 and 620 cm^{-1} are ascribed to aromatic $C-H$ bending vibrations (Pan et al. 2012).

Figure 7: Averaged FTIR spectra (auto-smoothed and auto-baseline corrected) of bio-oil obtained at optimized condition (a) organic phase; (b) aqueous phase

3.7 TGA of the organic phase bio-oil

Thermogravimetric analysis of bio-oil provides data on weight loss by evaporation as sample is heated over a certain temperature range. The resulting information similar to the distillation data, which can be used to estimate amount of bio-oil that will distill into specific fuel products. In this study, TGA analysis of commercial fossil premium motor spirit (PMS), kerosene and diesel was performed as standard. The organic bio-oil was subjected to the same thermal treatment. From Figure 8 (a), final evaporation temperature of PMS, kerosene and diesel was found to be 126, 185 and 291 ^{o}C respectively. Using the final evaporation temperature, by extrapolation, the organic phase bio-oil constitutes (Figure 8b) about 70wt% volatile fraction. The mass loss above 300 ^{o}C can be attributed to thermal decomposition of the residue. About 68 wt% of the oil has boiling range similar to that of diesel. Similarly, approximately 53 wt% of the bio-oil is made up of kerosene boiling fraction while 35 wt% has boiling characteristic comparable to that of PMS. Also, information from the TGA simulated distillation can also be used as an indicator for selecting temperature condition for GC-MS analysis of the oil. Based on the injection temperature selected (250 °C) for the bio-oil characterization, only about 62 % of the oil can be analyzed by the GC-MS.

3.8 GC-MS analysis of the organic phase bio-oil

Identification of detail chemical compounds in the bio-oil samples was carried out by GC-MS. Library search of twenty (20) most abundant compounds using MS NIST library 2011 showed that the organic phase (Table 8a) consists predominantly benzene derivatives such as phenols, methyl-phenol, ethyl-phenol, methoxy-phenols, methoxy-benzene, benzaldehyde and benzene carboxylic acid, which constitute accounted for about 60 % of the total organic phase, which is in strong agreement with the bio-oil composition reported by Lim et al (2016). Other compounds identified are hydrocarbons (dimethylcyclohexene and ethylbiphenyl). These together can be processed to fuels and valuable chemicals. The aqueous phase (Table 8b) comprised mainly organic acids, esters, ketones, aldehydes and oxygenated aromatics. The composition of organic phase bio-oil in this study is similar to the result of GC-MS analysis reported by Strezov et al. (2008). The oil analyzed by the author consisted large amount of benzene derivatives (24.46 wt%). The composition of bio-oil reported by Lee et al. (2010) was made up of 27.2 % organic acids, 7.9 % phenols, which is comparable to the aqueous phase composition in this study. Generally, the bio-oil aqueous phase is considered less important and often discarded as paralysis by-products due to lack of specific applications. However, recent studies have proposed production of hydrogen *via* catalytic aqueous, and steam reforming processes from this stream (Resende et al., 2015; Chan et al., 2015).

Table 8: GC-MS analysis of bio-oil (a) organic phase, (b) aqueous phase obtained at the optimized condition

3.9 GC analysis of the non-condensable gas

Samples of non-condensable gas were collected at different temperature (450, 600 and 750 ^oC) under the pyrolysis condition of 50 ^oC/min and 5 L/min N_2 as shown in Figure 9. The gas composition (nitrogen free basis) detected include hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). At 450 ^oC, the main components of the gas were CO_2 (16.42 vol%), H_2 (15.44 vol%) and CO (9.79 vol%). The high amount of CO_2 and H_2 and the release of CO are attributed to fragmentation and subsequent transformation of unstable carbonyl and carboxyl groups from depolymerization of holocellulose (hemicellulose and cellulose) and the resulting char transformation (Collard and Blin, 2014). The trace of CH_4 (0.84 vol%) detected at this temperature is mainly due to demethylation of char from hemicellulose and fragmentation of methoxy group of lignin. As the temperature increased, the amount of CO_2 declined considerably due to the fact that fragmentation of glyosidic bonds in the holocellulose must have been completed. This observation is in strong agreement with the TG/DTG result. A total of 14.04 and 12.56 vol% CO_2 was recorded at 600 and 750 ^oC respectively. The amount of CO_2 recorded at 450^{o}C (16.42 vol%) in this study is similar to the value (18.5% CO_2) reported by Strezov et al. (2008) during the pyrolysis of NG at 500 ^oC. Decline in the amount of CO_2 with increasing pyrolysis temperature has been reported by De Conto et al. (2016). The authors recorded CO_2 value of about 42.25 vol% at 500 ^oC, which declined substantially to around 12 vol % at 600 ^oC and then to about 9.vol% at 700 ^oC. The continuous rise in the CO, H_2 and CH_4 components of the non-condensable gas with pyrolysis temperature can be ascribed to carbon-carbon scission within the lignin and demethylation of final residue from the sample. This can also be attributed to the pyrolysis secondary reactions usually promoted by mineral elements in the biomass, particularly the alkali and alkali element (K, Ca) (Mohammed et al., 2016b). At 600

^{o}C, the amount of H_2, CO and CH_4 recorded was 25.32, 13.60 and 3.36 vol% respectively. This value increased to 35.45, 23.12 and 6.55 vol% correspondingly. The ratio of H_2/CO (vol%/vol%) increased from 1.58 to 1.86 at 450 to 600 ^{o}C and there after decreased to 1.53 at 750 ^{o}C. This indicate that the non-condensable gas from NG pyrolysis is a suitable feedstock for Fischer-Tropsch (FT) synthesis, where the syngas can be further processed into liquid fuel (Pirola et al., 2014; De Conto et al., 2016). However, presence of hydrogen sulfide (H_2S) in bio-syngas is a common characteristic of a non-condensable gas from biomass pyrolysis due to the presence of sulfur in the feedstock (Mohammed et al., 2015b). Catalyst used in the FT synthesis are highly sensitive to H_2S even at part per million level (Yamamoto et al., 2015). Gas cleaning is therefore need prior to the FT process. H_2S can be selectively removed from gas stream by absorption with the aid of selexol solvent (Mohammed et al., 2014a).

3.10 Characteristics of produced bio-char

Physicochemical properties of NGS bio-char produced at different temperature and 50 ^{o}C/min and 5 L/min nitrogen flow are summarized in Table 9. Volatile matter (VM) and heating value of the bio-char decreased with increasing pyrolysis temperature while the ash content (AC) and fixed carbon (FC) increased. This means that with increasing temperature, more VM is released and highly thermal stable and non-volatile components of the source biomass are left within the remaining solid. Reduction in the heating value is attributed to the increased AC, which is non-combustible and generally has negative impact on the solid fuel (Mohammed et al., 2014b). The ultimate analysis showed increased carbon content (C) with pyrolysis temperature while oxygen (O), and hydrogen (H) decreased (Table 9). This can be attributed to structural transformation of char via scission and cracking of weak bond within the bio-char structure. Similarly, nitrogen (N) and sulfur (S) content also declined with pyrolysis temperature. This shows that N and S compounds are released during pyrolysis (De Conto et al., 2016), which is responsible for the sulfur and nitrogenous compounds detected in the bio-oil (Table 8).

Thermal stability of bio-char can be evaluated from the proximate, ultimate and TGA analyses. De Conto et al. (2016) reported that the ratio of FC to the sum of FC and VM [FC/ (VM+FC)] of bio-char is an indicator of thermal stability. A ratio between 0.78 and 0.85 were recorded in this study, which indicates high thermal stability of organic matter in the bio-char. Spokas (2010), reported that there is connection between bio-char stability and O/C molar ratio. The author stated that O/C ratio below 0.2 signifies a minimum bio-char half-life of 1000 years. In this study, O/C mole ratio of 0.22, 0.15 and 0.09 was observed for the bio-char produced at 450, 600 and 750°C respectively. Similarly, Harvey et al. (2012) proposed a recalcitrance index (R_{50}) for evaluating bio-char suitability for carbon sequestration. The authors defined R_{50} as the ratio of temperature of bio-char ($T_{50\ \text{bio-char}}$) to temperature of graphite ($T_{50\ \text{graphite}}$) at which both materials decompose 50% initial weight under oxygen atmosphere. They grouped bio-char based on the R_{50} value into class A ($R_{50} \geq 0.70$), B ($0.50 \leq R_{50} < 0.70$) or C ($R_{50} < 0.50$) where class A, B and C represent carbon sequestration potential similar to graphite, intermediate sequestration potential and carbon sequestration potential similar to the biomass plant. Thermal decomposition of the produced bio-char in oxygen atmosphere (50 mL/min) was carried out from ambient to 900 °C at 10 °C/min (Figure 10). Thermal stability increased with pyrolysis temperature. Decomposition of the bio-char produced at pyrolysis temperature of 450, 600 and 750 °C commenced at 250, 309 and 320 °C respectively. The corresponding $T_{50\ \text{bio-char}}$ was 380, 385 and 392 °C. Using 886 °C for $T_{50\ \text{graphite}}$ (Harvey et al., 2012), the equivalent R_{50} value was 0.43, 0.43 and 0.44. Hence, the bio-chars from NGS in this study are class C and have potential carbon sequestration similar to the uncharred biomass plant. Also, the TGA result indicate that the char can be used in processes under moderate temperature up to 300 ^{o}C. Residue (non-combustible) from the TGA profile (Figure 10) increased with temperature pyrolysis temperature. This observation is in good agreement with the proximate analysis results particular the increased ash content observed with pyrolysis temperature.

Scanning electron micrograph and elemental mapping of the bio-char (Figure 11) showed that the materials have porous structures, which increased with pyrolysis temperature. This result was further confirmed using physisorption analysis. The specific surface area recorded for the bio-char produced at 450, 600 and 750 ^{o}C was 0.014, 0.126 and 0.293 m^{2}/g and the corresponding pore volume of 0.08, 010 and 0.13cm^{3}/g was observed. From elemental mapping of the bio-char (Figure 11), potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P) and chlorine (Cl) constitute the major mineral elements in the bio-char, which originated from the source biomass. K, Ca, Mg and P are macronutrients needed for most plant growth. Bio-char can therefore be applied as a source of macronutrient for agricultural production.

4. Conclusions

Pyrolysis of Napier grass was carried out in a vertical fixed bed tubular reactor. Optimization of process variables such as temperature, heating rate and nitrogen flow rate was performed by means of central composite design approach. The individual model equation for bio-oil, bio-char and non-condensable gas yield was developed using set of experimental data and analysis of variance. Temperature, nitrogen flow rate and heating rate had significant impact on the bio-oil and non-condensable gas yield while the bio-char yield was mainly affected by the pyrolysis temperature.. The oil yield was maximized by optimizing the process variables and optimum bio-oil yield of 51.94 wt% was predicted at 600 ^{o}C, 50 ^{o}C/min and 5 L/min nitrogen flow. This result was further validated through multiple experiments and the average value of the experimental results was in good agreement with the predicted value. Therefore, it can be inferred that the developed quadric model for bio-oil yield is adequate. The optimum bio-oil yield recorded in this study is higher than the pyrolysis oil yield derived from Napier grass reported in the literature. The bio-oil obtained throughout was two-phase liquid, the organic phase (high molecular weight component) and aqueous phase (low molecular weight component). Both phases collected at optimized condition were characterized using standard analytical techniques. The results revealed that the organic phase consists mainly various benzene derivatives and hydrocarbons which can be further processed into fuels and valuable chemicals while the aqueous phase was predominantly water, acids, ketones, aldehydes and some phenolics and other water-soluble organics. The non-condensable gas was made-up of methane, hydrogen, carbon monoxide and carbon dioxide with high hydrogen/carbon monoxide ratio suitable for Fischer-Tropsch (FT) synthesis. Biochar collected was a porous carbonaceous material, rich in mineral elements, which may be used as adsorbent, solid fuel or source of macronutrient for agricultural production. The bio-char also possessed potential for carbon sequestration. This study demonstrated that Napier grass biomass is a potential feedstock for production of high-value bioenergy precursors.

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