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Optimization using response surface methodology and
pyrolysis products characterization**

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

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15 **Abstract**

16 This study presents first optimization report on pyrolysis oil derived from Napier grass. Effects
17 of temperature, heating rate and nitrogen flow rate on the intermediate pyrolysis of Napier grass
18 biomass in a vertical fixed-bed tubular reactor were investigated collectively. Response surface
19 methodology with central composite design was used for modelling the process and optimization
20 of the process variables. Individual second order polynomial model was found to be adequate in
21 predicting bio-oil, bio-char and non-condensable gas yield. The optimum bio-oil yield of 50.57
22 wt% was recorded at 600 °C, 50 °C/min and 5 L/min nitrogen flow. The bio-oil obtained
23 throughout this study was two-phase liquid, organic and aqueous phase. The bio-oil, bio-char and
24 non-condensable gas were characterized using standard analytical techniques. The results
25 revealed that the organic phase consists of hydrocarbons and various benzene derivatives, which
26 can be further processed into fuels and valuable chemicals. The aqueous phase was
27 predominantly water, acids, ketones, aldehydes and some phenolics and other water-soluble
28 organics. The non-condensable gas was made up high hydrogen/carbon monoxide ratio suitable

29 for liquid fuel synthesis via Fischer-Tropsch Synthesis. The bio-char was a porous carbonaceous
30 material with high energy content, which can be applied as a solid fuel, adsorbent or source of
31 biofertilizer. This study demonstrated that Napier grass biomass is a viable feedstock for
32 production of high-value bioenergy precursors.

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

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36 1. Introduction

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

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

51 Miscanthus, switchgrass, the biomass yield is between 10 and 20 oven dry tons per hectare per
52 annum and require some nutrient input during cultivation ([Richter et al., 2008](#); [Cadoux et al.,](#)
53 [2012](#)). [Flores et al. \(2012\)](#) reported that Napier grass can be grown without any nutrient or
54 fertilizer input. They evaluated the performance of two Napier grass species with and without
55 application of nitrogen fertilizer under the Cerrado climatic condition (semi-humid tropical
56 climate). Their findings revealed that the biomass yield was between 30 to 42 oven dry tons per
57 hectare and showed no response to nitrogen fertilization. Recent study on environmental and
58 economic benefit analysis of Napier grass has been reported by [Tsai and Tsai \(2016\)](#). Their result
59 shows that Napier grass can mitigate CO₂ emissions to the order of 5 million Gg per annum. The
60 energy equivalent was found to be 11 million barrels per 100 000 hectare annually which equals
61 to 110 barrels of oil energy equivalent per hectare. This value strongly agrees with the findings
62 reported by [Samson et al. \(2005\)](#) and [Flores et al. \(2012\)](#). Cultivation of Napier grass follows
63 conventional farming practices. It outcompetes weeds and therefore, requires lower
64 establishment costs. This makes it one of the best potential energy crops for the development of
65 efficient and economic bioenergy systems ([Samson et al., 2005](#); [Flores et al., 2012](#)). Recently,
66 investigations have also shown that Napier grass can be incorporated into tree plantations such as
67 oil palm, rubber tree plantations where there are large areas of unused spaces, estimated at
68 26.63% of the total space ([Zhou et al., 2012](#); [Mohammed et al., 2015a](#)). [Mohammed et al.](#)
69 [\(2015a\)](#) reported that intercropping Napier grass with oil palm produce thick elongated Napier
70 grass stem, which contained more biomass than the Napier grass grown under unshaded
71 conditions. This therefore offers another economic benefit.

72 Pyrolysis is the thermal decomposition of biomass in total absence of oxygen to produce solid,
73 liquid and gas products. This process has high improved efficiency, environmental suitability and

74 flexibility as virtually any biomass type can be handled to generate various products
75 ([Heidenreich and Foscolo, 2015](#); [Mohammed et al., 2016c](#)). In addition, high liquid yield (known
76 as bio-oil) which is of most interest can be obtained through pyrolysis process under a careful
77 control of process variables such as inert gas flowrate, pyrolysis temperature, heating rate, vapor
78 residence time, reactor type, and the temperature regime between the reaction and cooling zone
79 ([Bridgwater, 2012](#); [Eom et al., 2012](#)). Generally, pyrolysis process is classified into slow,
80 intermediate and fast pyrolysis. In slow pyrolysis (carbonization), temperature up to 400 °C,
81 vapor residence time of 60 minutes to days are used and a typical product yield of about 35 %
82 bio-char, 30 % bio-oil, and 35 % non-condensable gas. For fast pyrolysis, temperature of about
83 500 °C, high heating rate (up 1000 °C/min) and short vapor residence time of approximately 1 s
84 are applied. Nearly 80 % bio-oil yield (wet basis), and about 13 and 12 % non-condensable gas
85 and bio-char are obtained. ([Bridgwater, 2012](#); [Mohammed et al., 2015b](#)). On the other hand,
86 intermediate pyrolysis produces about 40-60 % bio-oil, 15-25 % bio-char and 20-30 % non-
87 condensable gas under process condition of 500-650 °C and 10 to 30 s vapor residence time.
88 Intermediate pyrolysis has added advantages over the fast pyrolysis in that the oil from it is less
89 reactive and may be used directly as fuel in engines and boilers. It also produces dehydrated
90 char, which can be used for both agricultural and energy applications ([Tripathi et al., 2016](#);
91 [Mohammed et al., 2016c](#)). However, production of bio-oil from biomass via pyrolysis requires
92 energy at different stages. Energy is consumed during biomass collection, bio-oil production
93 stage (size reduction, feeding, pyrolysis and cooling) and bio-oil transportation. Study has shown
94 that about 82 % of the total energy requirement for a bio-oil production process is consumed at
95 the production stage mainly during size reduction and pyrolysis (high temperature is needed to
96 decompose the biomass) ([Ning et al., 2013](#)). Though, the challenge of high energy requirement

97 may be compensated through efficient utilization of other pyrolysis products (bio-char and non-
98 condensable gas). Climate change mitigation is an unresolved issue between the cons and pros of
99 biofuels utilization. Production of biofuel can be said to reduce greenhouse gases only when it
100 produce residuals that render the use of fossil fuels unnecessary. Consequently, production of
101 second generation biofuels should be carefully synchronized to encourage more agricultural food
102 production and the use of marginal lands for cultivation of energy crops in order to develop a
103 sustainable bioenergy system (Caputo, 2014).

104 Utilization of Napier grass for the development of biofuels via pyrolysis is very limited. Strezov
105 et al. (2008) reported thermochemical conversion of Napier grass to bio-oil, bio-char and non-
106 condensable gas using a pyro-probe type reactor. They investigated effect of heating rate (10 and
107 50 °C/min) on the pyrolysis product distribution. In each case, the system was ramped to a
108 maximum temperature of 900 °C. Their result showed that the bio-oil collected was made up of
109 organic acids, phthalate esters, and larger fraction of various benzene chemicals, phenols and
110 pyrans. They reported that the high heating rate of 50 °C/min promoted the formation of smaller
111 acids and benzene fractions in the bio-oil compared to the low heating rate of 10 °C/min. CO₂
112 was found to be the major component in the non-condensable gas. They stated that the bio-oil
113 collected was a two-phase liquid and sample was analyzed with GC-MS without separation into
114 individual phases. Although, a mixture of methanol and chloroform was used as solvent but there
115 is high tendency of phase separation during the GC-MS analysis and the sample injected may not
116 be the true representation of the whole bio-oil. Lee et al. (2010) reported pyrolysis of Napier
117 grass in an induction-heating reactor. They investigated effect of heating rate between 50 and
118 200 °C/min and biomass particle size within 2 mm at pyrolysis temperature of 500 °C. Their
119 findings also showed that bio-oil yield increased with heating rate from 50 to 150 °C/min but

120 declined thereafter. Maximum bio-oil yield of 36 wt% was reported at 150 °C/min with 0.224
121 mm biomass particle size. The bio-oil yield was lower than those generally obtained from a fast
122 pyrolysis system (50-60 wt%) and was attributed to the low level of heating rate used compared
123 to the fast pyrolysis where up to 1000 °C/min is normally employed. This conclusion may not be
124 valid as the study was conducted under a constant temperature of 500 °C, which may not be the
125 optimum temperature for complete devolatilization of various structural components in the
126 biomass. Pyrolysis product distribution is strongly related to the pyrolysis temperature and vapor
127 residence time in the reactor compared to the heating rate ([Bridgwater, 2012](#); [Mohammed et al.,
128 2015b](#)). Their findings also reveal that the bio-oil was predominantly acetic acid, phenols,
129 ketones, and nitrogenated hydrocarbons. These chemical species are polar compounds that are
130 generally present in the aqueous phase of the bio-oil. The major composition of the non-
131 condensed gas reported were furans, olefins and mono-aromatic hydrocarbons (benzene, toluene
132 and xylene), which are normal component of the condensate. This means that the cooling system
133 used during the study was inefficient. Thus, the composition of the bio-oil reported does not
134 represent the whole condensables from the Napier grass.

135 A study recently conducted by [Sousa et al. \(2016\)](#) on pyrolysis of Napier grass in a fluidized bed
136 reactor with a feed rate between 20 and 35 kg/h, temperature at around 500 °C. Maximum oil
137 yield of 28.2 % was recorded. This yield was also far lower relative to a typical bio-oil yield (40-
138 60 %) from a fluidized bed pyrolysis system. The authors attributed it to the accumulation of
139 heavier fractions within the system before the cooling zone. The bio-oil composition reported
140 had principally phenolics, organic acids and traces of levoglucosan and mono-aromatic
141 hydrocarbons. H₂, CO, CO₂, CH₄ and C₂H₆ were the main component detected in the non-
142 condensable gas. However, the yield and composition of the bio-oil collected may have been

143 affected as the authors stated that air was employed as the fluidizing gas instead of an inert gas.
144 Effect of other temperature levels and variations in the fluidizing gas velocity were not
145 investigated. Similarly, [De Conto et al. \(2016\)](#) studied pyrolysis of Napier grass in a rotary kiln
146 reactor where the effect of pyrolysis temperature and rotating speed of the reactor were
147 investigated. Information regarding the bio-oil collected by the authors was only limited to the
148 yield. Physicochemical properties and chemical compositions of the bio-oil were not determined.
149 The non-condensable gas analyzed particularly at 600 °C was made up of high hydrogen
150 (H₂)/carbon monoxide (CO) ratio which was attributed to the temperature only. However, this
151 may be a combined effect of temperature and vapor residence time in the reactor. From the
152 reactor size and carrier gas flowrate reported by the authors, vapor residence was around 1.425
153 min (85 sec), which is long enough to result to severe secondary cracking of the pyrolysis vapor
154 at such a high temperature. Some classical studies on the pyrolysis of Napier grass have also
155 been reported by our research group recently ([Mohammed et al., 2015b](#); [Lim et al., 2015](#),
156 [Mohammed et al., 2016a](#), [2016b](#), [2016d](#), [Lim et al., 2016](#)). To date, no study on pyrolysis of
157 Napier grass is available in the literature that deals with collective examination of pyrolysis
158 temperature, heating rate, inert gas flowrate on the products distribution and composition. This
159 investigation is needed in order to appropriately evaluate the energy potential of the biomass.

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

164 2. Materials and Methods

165 2.1 *Material and characterization*

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

181 2.2 *Pyrolysis experiment*

182 Intermediate pyrolysis study was carried in a vertical tube fixed bed pyrolysis system as shown
183 in Figure 1. The system consists of a fixed bed reactor made of stainless steel (115 cm long, 6 cm
184 inner diameter), a distribution plate with 1.5 mm hole diameter which sits at 25 cm from the
185 bottom of the tube, two nitrogen preheating sections, a cyclone, water chiller operating at 3 °C

186 attached to a coil condenser, oil collector and gas scrubbers. 200 g of NGS (bone dry, 2.5 mm
 187 particle size) was placed on the distribution plate inside the reactor tube and pyrolysis was
 188 conducted under nitrogen atmosphere. The reaction temperature was monitored with a K-type
 189 thermocouple connected to a computer through data logger. The reaction time was kept at 60 min
 190 after the temperature reaches the desired value. The pyrolysis vapor was condensed by passing
 191 through a condenser connected to a chiller at 3 °C and the oil was collected. The bio-oil, bio-char
 192 and non-condensable gas yield was computed according to equation (1), (2) and (3) respectively.
 193 20 sets of pyrolysis experiments were conducted based on the number generated by the statistical
 194 software where the pyrolysis temperature (450-750 °C), nitrogen flow rate (5-25 L/min) and
 195 heating rate (10-50 °C/min) were selected in this study.

196
$$\text{Yield [wt\%]}_{\text{bio - oil}} = \left[\frac{\text{weight of the bio - oil collected}}{\text{weight of biomass feed}} \times 100 \right] \text{----- (1)}$$

197
$$\text{Yield [wt\%]}_{\text{bio - char}} = \left[\frac{\text{weight of the bio - char collected}}{\text{weight of biomass feed}} \times 100 \right] \text{----- (2)}$$

198
$$\text{Yield [wt\%]}_{\text{non - condensable gas}} = 100 - \left(\text{Yield [wt\%]}_{\text{bio - oil}} + \text{Yield [wt\%]}_{\text{bio - char}} \right) \text{----- (3)}$$

199

200

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

205

206 2.3 *Response surface methodology (RSM)*

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

218
$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \text{-----} (4)$$

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

221
$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^n \sum_{j>1}^n \beta_{ij} X_i X_j \text{-----} (5)$$

222
 223 Where Y is the predicted response, n is the number of experiments, β_0 , β_i , β_{ii} and β_{ij} is regression
 224 coefficients for the constant, linear, quadratic and interaction terms, respectively. X_i and X_j are
 225 the coded independent factors. The adequacy of the final model was tested using both graphical

226 and numerical analysis and the experimental data were analysed statistically using analysis of
227 variance (ANOVA).

228 **Table 1:** Range of independent variables and experimental levels

229

230 2.4 *Pyrolysis products characterizations*

231 Pyrolysis oil collected at optimized condition was further analyzed. Physicochemical properties
232 of the bio-oil such as pH, water content, calorific value, density and viscosity were analyzed with
233 a WalkLAB microcomputer pH meter (TI9000, Trans Instruments, Singapore), Karl Fischer V20
234 volumetric titrator (Mettler Toledo, Columbus, OH, USA), oxygen bomb calorimeter (Parr 6100,
235 Parr Instruments, Molin, IL, USA), Anton Paar density meter (DMA 4500 M, Ashland, VA,
236 USA) and Brookfield viscometer (DV-E, Hamilton, NJ, USA) respectively. Carbon, hydrogen,
237 nitrogen, sulfur and oxygen contents of the bio-oil were determined with a CHNS/O Analyzer
238 (2400 Series II CHNS/O analyzer, Perkin Elmer Sdn Bhd, Selangor, Malaysia). Functional group
239 analysis was performed with fourier transform infrared-FTIR (Spectrum RXI, PerkinElmer,
240 Selangor, Malaysia) using a pair of circular demountable potassium bromide (KBr) cell windows
241 (25mm diameter and 4mm thickness). Spectra were recorded with Spectrum V5.3.1 software
242 within wave number range of 400-4000 cm^{-1} at 32 scans and a resolution of 4 cm^{-1} . Fractionation
243 of the organic phase bio-oil was simulated using TGA in nitrogen atmosphere at 20mL/min,
244 10°C/min from ambient to 500°C to examine the volatile fractions and the result was compared with
245 the simulated distillation of fossil-gasoline, kerosene and diesel. Detail of the chemical composition
246 of the bio-oil was determined using a gas chromatograph-mass spectrometer (GC-MS)
247 (PerkinElmer Clarus[®] SQ 8, Akron, OH, USA) with a quadruple detector and column (30m x
248 0.25mm x 0.25 μm) (PerkinElmer-Elite[™]-5ms, Akron, OH, USA). The oven was programmed at
249 an initial temperature of 40 °C, ramp at 5 °C /min to 280 °C and held there for 20 min. The

250 injection temperature, volume, and split ratio were 250 °C, 1 µl, and 50:1 respectively. Helium
251 was used as carrier gas at a flow rate of 1 mL/min. The peaks of the chromatogram were
252 identified by comparing with standard spectra of compounds in the National Institute of
253 Standards and Technology library (NIST, Gaithersburg, MD, USA).

254 Samples of the non-condensable gas were collected in SKC polypropylene fitted gas sampling
255 bag and analyzed offline with a gas chromatography (PerkinElmer Clarus 500, Akron, OH,
256 USA) equipped with stainless steel column (Porapak R 80/100) and thermal conductivity
257 detector (TCD). Helium was used as a carrier gas and the GC was programmed at 60 °C, 80 °C and
258 200 °C for oven, injector and TCD temperature respectively. Bio-char proximate and ultimate
259 analyses were performed following the same analytical procedure adopted for the feedstock
260 characterization above. Scanning electron microscopy (SEM, FEI Quanta 400 FE-SEM,
261 Hillsboro, OR, USA) and physisorption analyzer (ASAP 2020 Micrometrics, Norcross, GA,
262 USA) were used to evaluate the surface and structural characteristics, and specific surface area
263 (BET) and pore properties of the bio-char respectively.

264 **3. Results and Discussion**

265 *3.1 Feed stock characteristics*

266 Characteristic of NGS used in this study is summarized in Table 2. The proximate analysis result
267 obtained showed significant difference relative to similar properties of Napier grass (NG)
268 reported in the literature. Higher volatile matter and lower ash contents were recorded compared
269 to the values reported by [Strezov et al. \(2008\)](#), [Lee et al. \(2010\)](#), [Braga et al. \(2014\)](#) and [De](#)
270 [Conto et al. \(2016\)](#). Higher heating value (HHV) was 18.05 MJ/kg relative to 15.61 MJ/kg and
271 15.77 MJ/kg reported by [Braga et al. \(2014\)](#) and [De Conto et al. \(2016\)](#) respectively. These
272 variations in the proximate analysis result is attributed to the post-harvest treatment of the NG

273 sample used. The results of ultimate and structural analyses (Table 2) showed good agreement
274 with the literature values. Comparing the structural characteristics of NGS with that of
275 switchgrass and miscanthus, from the work of [Imam and Capareda \(2012\)](#) and [Rena et al. \(2016\)](#),
276 switchgrass has lower cellulose (32-34 wt%) and lignin (18.8 wt%) contents. Similarly,
277 miscanthus has lower lignin content (12-12.58 wt%) but higher cellulose (50.34-52.13 wt%) and
278 hemicellulose (24.83-25.76 wt%) contents as reported by [Brosse et al. \(2012\)](#) and [Shemfe et al.](#)
279 [\(2016\)](#). Studies on the detail mineral composition of NG biomass is rarely reported. This
280 characteristic is very important for biomass thermochemical conversion. For pyrolysis, it has
281 been reported that mineral composition of biomass has great influence on both product yield and
282 bio-oil composition ([Mohammed et al., 2016b](#)). Most researchers employed x-ray fluorescence
283 (XRF), energy dispersive x-ray (EDX) in determining the mineral composition of biomass.
284 These techniques provide elemental composition at a specific point within the sample instead of
285 the mineral distribution in the whole sample. [Strezov et al. \(2008\)](#) reported silicon (Si),
286 potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), aluminum (Al) and sodium (Na) using
287 XRF as the major elements present in the Napier grass biomass. In this study, the major elements
288 recorded in the feedstock using atomic absorption spectrometer (AAS) showed similar
289 mineralogical composition (Na, K, Ca, Al, Fe and Si).

290

291 **Table 2:** Characteristics of Napier grass biomass used

292

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

296 °C. Pyrolysis of a lignocellulosic biomass proceeds through simultaneous decomposition of
297 hemicellulose, cellulose and lignin of the biomass with each component displaying separate
298 mechanism, which makes the process so complex (Kan et al., 2016; Anca-Couce, 2016). Most
299 studies have focused on the classical evaluation of degradation of the individual components as a
300 foundation of the likely decomposition pathway. However, research have shown that there is
301 interaction between the structural components of the biomass during pyrolysis, which is also
302 affected by the mineral content of the biomass (Kan et al., 2016; Anca-Couce, 2016). In this
303 study, pyrolysis profile of NGS from the TG/DTG showed four distinct regions at temperature
304 around 200 °C, 229-285 °C, 326 °C and 373-540 °C. Visible peak at about 200 °C was observed,
305 which is due to the decomposition of extractives. This could also be due further dehydration of
306 the biomass through cleavage of hydroxyl groups in the hemicellulose, cellulose and lignin (Van
307 de Velden et al., 2010; Collard and Blin, 2014). The total weight loss recorded under this region
308 was 12.58 wt%. A shoulder is observed at temperature between 229 and 285 °C and is ascribed
309 to the fast decomposition of hemicellulose as a result of cleavage of the glycosidic bond between
310 the monomeric units. Depolymerization of cellulose to active cellulose is also expected within
311 this temperature range (Van de Velden et al., 2010; Collard and Blin, 2014). The corresponding
312 weight loss of 13.66 wt% was recorded. The main characteristic peak was observed at 326 °C.
313 This is attributed to cellulose decomposition and had a maximum weight loss of 35.74 wt%.
314 Temperature between 373 and 540 °C represent degradation of lignin due to carbon-carbon
315 scission and disruption of aromatic rings within the lignin structure, which resulted in weight
316 loss of 10.78 wt%. Temperature beyond 540 °C represent transformation of the remaining solid
317 (char) through aromatization and demethylation (Patwardhan et al., 2011; Collard and Blin,
318 2014). Similar decomposition profile of NG has also been reported by Braga et al. (2014). They

319 ascribed peaks observed at temperature range of 180-300 °C, 300-380 °C and 380-530 °C to the
 320 decomposition of hemicellulose, cellulose and lignin respectively. Similarly, [De Conto et al.](#)
 321 [\(2016\)](#) studied thermogravimetrics of NG and reported decomposition of cellulose at 318 °C and
 322 lignin with 350-500 °C. These decomposition temperature ranges has also been reported in the
 323 literature for other lignocellulosic biomass ([Gómez et al., 2016](#))

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

325
 326 *3.2 Central composite design (CCD) and statistical analysis*

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

333
$$Y_{\text{bio-oil}} = 49.37 + 2.03A - 0.70B + 2.04C - 13.31A^2 + 0.75B^2 - 0.83C^2 - 0.67AB - 1.88AC + 0.09BC \text{-----} (6)$$

334
$$Y_{\text{bio-char}} = 21.78 - 11.89.A + 0.66B - 0.73C + 10.32A^2 - 0.14B^2 - 0.72C^2 - 0.61AB + 0.27AC - 0.52BC \text{-----} (7)$$

335
$$Y_{\text{Non-condensable-gas}} = 28.85 + 9.85.A + 0.04B - 1.31C + 2.99A^2 - 0.61B^2 + 1.55C^2 + 1.28AB + 1.61AC + 0.43BC \text{---} (8)$$

336
 337 **Table 3:** CCD Experimental Design Matrix and Response

338

339 For the bio-oil yield, the Model F-value of 171.60 (Table 4a) implies the model is significant.
340 Lack of Fit F-value of 3.18 implies that it is not significant relative to the pure error.
341 Nonsignificant lack of fit is desirable because it is wanted to fit. For the bio-char and non-
342 condensable gas yield, similar trends are observed. Model F-value of 151.22 (Table 4b) and
343 69.74 (Table 4c) with the corresponding lack of fit F-value of 1.47 and 3.41 are recorded.
344 Values of "Prob > F" less than 0.0500 indicates model terms are significant while values greater
345 than 0.1000 indicate the model terms are not significant.
346 In the case of bio-oil, the significant model terms are A, B, C, A², AB, AC, with the
347 corresponding F-value of 62.92, 7.46, 63.59, 741.20, 5.52, and 43.12. It can also be observed
348 that the most significant model term on the bio-oil yield obeyed the following order
349 A²>A>C>AC>B>AB while the quadratic terms B², C² and the interaction BC does not have a
350 significant impact on the bio-oil yield. For bio-char, the significant model terms are A and A²
351 with the linear term having the largest significance due higher F-value of 1006.27 (Table 4b).
352 The significant model terms for the non-condensable gas are A, C, A², AB, AC, with A being the
353 most significant term having F-value of 557.41 (Table 4c). The coefficient of determination, R²
354 for the bio-oil, bio-char and non-condensable gas model is 0.9936, 0.9927 and 0.9843
355 respectively (Table 4a-c). Another regression parameter considered is the adjusted R², which
356 improves the coefficient of determination (R²) in relation to the sample size and the model terms,
357 and the corresponding value is 0.9878, 0.9861 and 0.8903. The R² and adjusted R² values for the
358 individual model are high enough and comparable, which indicate that the selected quadratic
359 response surface model for the pyrolysis products sufficiently describe the experimental data
360 within the selected operating conditions. Also, the predicted R² value of the bio-oil, bio-char and
361 the non-condensable gas model is 0.9518, 0.9411 and 0.8903 respectively which is in good

362 agreement with the respective adjusted R^2 values. Adequate precision (Adeq Precision) is a
363 measure of signal to noise ratio and a ratio greater than 4 is desirable. In this study, the value of
364 Adeq precision is 36.4925, 32.8072 and 27.3167 for the bio-oil, bio-char and non-condensable
365 gas model respectively. These high values indicate adequate signal and the models can be used to
366 navigate the design space. Furthermore, the coefficient of variation (CV) which is a measure of
367 the reliability of the experiment, it expresses the overall experimental error as a percentage of the
368 overall mean. The CV value recorded for the pyrolysis products is less than 4.5, hence, this
369 experiment can be said to be highly reliable since the lower the CV value, the higher is the
370 reliability of the experiment.

371

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

374

375 3.3 *Model validation and response surface plot*

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

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

387

388 In order to examine the effect of the pyrolysis process variables on the response values,
389 interaction and 3D surface plots were used. Although, it is not possible to present the effects of
390 all the parameters studied on the same 3D, as such, the response surface plots are presented by
391 varying two factors and keeping one factor constant as shown in Figure 4(a-f), 5(a-f) and 6(a-f)
392 for bio-oil, bio-char and non-condensable gas yields respectively. The interaction between the
393 nitrogen flow and temperature at a constant heating rate (30 °C/min) on the bio-oil yield (Figure
394 4a-b) shows that increase in the nitrogen flow rate from 5 L/min to 25 L/min and temperature
395 from 450°C to 600 °C increased the bio-oil yield. The oil yield became maximum at 600 °C for
396 both nitrogen levels but at a different amount. Lower nitrogen level (5 L/min) produced 52.06
397 wt% oil compared to 49.20 wt% oil yield at 25 L/min nitrogen flow at the same 600 °C. The
398 decreased oil yield at the higher nitrogen flow rate could be as a result of more uncondensed
399 volatiles leaving as part of non-condensable gas due to short vapor residence time in the
400 condenser. Declines in the oil yields were observed at temperature above 600 °C. The bio-oil
401 yield trend recorded with temperature from 450 °C to 600 °C and above 600 °C can be
402 respectively ascribed to degradation of more lignin, and secondary reactions of pyrolysis vapor
403 and more decomposition of bio-char at the elevated temperature (Soetardji et al., 2014). The
404 effect of heating rate and temperature on the bio-oil yield at a constant nitrogen flow rate (15
405 L/min) is presented in Figure 4c-d. Increasing temperature from 450 to 600 °C and heating rate
406 between 10 and 50 °C/min increased the oil yield from 29.26 to 46.13 wt% and 37.12 to 50.89
407 wt% respectively. The yield of more bio-oil at 50 °C/min relative to 10 °C/min under the same
408 pyrolysis temperature is attributed to rapid depolymerization of the biomass to primary volatiles

409 at the higher heating rate. (Yorgun and Yildiz, 2015). The oil yield decreased to 37.10 wt% at
410 both heating rates under the same temperature (750 °C) and nitrogen flow (15 L/min) due to
411 secondary reactions at such a high temperature. The combined effects of heating rate and
412 nitrogen flow rate at a pyrolysis temperature of 600 °C on the bio-oil yield is shown in Figure 4e-
413 f. As the nitrogen flow increased from 5 L/min to 25 L/min, bio-oil yield at 50 °C/min heating
414 rate remained higher compared to the oil collected at 10 °C/min but no significant impact of
415 nitrogen flow was observed in both cases. Bio-oil yield at 50 °C/min was between 50.72 and
416 51.94 wt% relative to 46.45-48.03 wt% oil recorded at 10 °C/min.

417 **Figure 4:** Interaction graphs and the corresponding surface response plots for the combined
418 effects of process variables on bio-oil yield. (a) and (b) effect of nitrogen flow and
419 temperature at 30°C/min; (c) and (d) effect of heating rate and temperature at
420 15L/min N₂; (e) and (f) effect heating rate and nitrogen flow at 600°C

421

422 Impacts of pyrolysis temperature, heating rate and nitrogen flow rate on the yield of bio-char are
423 shown in Figure 5 (a-f). Interactions between temperature and nitrogen flow Figure 5 (a-b)
424 showed that the temperature had great influence on the bio-char yield compared to the nitrogen
425 flow rate. A general decline in the bio-char yield was recorded with increasing temperature at
426 both 5 L/min and 25 L/min nitrogen flow rates, which is attributed to devolatilization more
427 organic materials as dehydration of hydroxyl groups and decomposition of lignocellulose
428 structure progresses with increasing temperature (Mohammed et al., 2015b). This clearly
429 demonstrated that bio-char yield is governed by the pyrolysis temperature. The impact of
430 temperature also dominated interaction between temperature and heating rates on the bio-char
431 yield (Figure 5c-d). There was no considerable difference between the bio-char yields at 10
432 °C/min and 50 °C/min throughout the investigated temperature range. Bio-char yields recorded

433 were 44.27 wt% and 42.27 wt% at 450 °C, and 20.59 wt% and 19.03 wt% at 750 °C for 10
434 °C/min and 50 °C/min heating rate respectively. The slightly lower value of bio-char recorded at
435 50 °C/min could also be attributed to rapid degradation of biomass. Influence of heating rate and
436 nitrogen flow on the bio-char yield is presented in Figure 5(e-f). Both factors did not
437 significantly impacted on the char yield. As nitrogen flow increased from 5 L/min to 25 L/min,
438 bio-char yield at 50 °C/min remained the same (around 20 wt %) while between 20.48 to 22.84
439 wt% char yield was recorded at 10 °C/min under the same nitrogen flow regime. These
440 observations indicated that the range of nitrogen flow rates used in this study was sufficient in
441 preventing secondary reaction such as condensation which normally favored char formation
442 (Yorgun and Yildiz, 2015).

443 **Figure 5:** Interaction graphs and the corresponding surface response plots for the combined
444 effects of process variables on bio-char yield. (a) and (b) effect of nitrogen flow and
445 temperature at 30°C/min; (c) and (d) effect of heating rate and temperature at
446 15L/min N₂; (e) and (f) effect heating rate and nitrogen flow at 600°C

447

448 Effects of process variables on the production of non-condensable gas are shown in Figure 6 (a-
449 f). The interaction between temperature and nitrogen flow (Figure 6a-b) revealed that non-
450 condensable gas yield increased with temperature at both nitrogen flow levels. As the
451 temperature progressed from 450 to 600 °C, the increase in the gas yield was not significant
452 under 5 L/min nitrogen flow. This indicates the most of the volatiles generated during the
453 pyrolysis are effectively captured in the condenser, which eventually ended up in the bio-oil as
454 rightly identified in the bio-oil yield section above. The significant change in the gas yield
455 recorded under 25 L/min nitrogen flow between 450 and 600 °C is mainly due to shorter vapor
456 residence time in the condenser compared to the 5 L/min nitrogen flow rate. With increasing

457 temperature above 600 °C, the gas yield increased rapidly in both nitrogen flow regimes, which
458 can be ascribed to further thermal decomposition of pyrolysis vapor in addition to some
459 uncondensed volatiles leaving the pyrolysis system as part of non-condensable gas, particularly
460 at the higher flow rate. 30.21-42.40 wt% gas yield was recorded with 25 L/min nitrogen flow
461 relative to 26.05-39.77 wt% gas yield using 5 L/min. Furthermore, the combined effects of
462 temperature and heating rate on the yield of non-condensable gas (Figure 6c-d) also revealed that
463 the temperature has great influence on the gas yield. With increasing temperature from 450-750
464 °C, the non-condensable gas yield increased from 26.46 to 42.94 wt% and 20.62 to 43.55 wt% at
465 10 °C/min and 50 °C/min respectively. This trend is believed to be as a result of secondary
466 cracking of volatiles and further decomposition of bio-char at higher temperatures (Yorgun and
467 Yildiz, 2015). On the other hand, nitrogen flow and the heating rate seem to have no considerable
468 impact on the yield of non-condensable gas (Figure 6e-f). As the nitrogen flow rate increased
469 from 5L/min to 25L/min, the change in the yield of non-condensable gas was insignificant at
470 both 10°C/min and 50°C/min. Gas yield of 28.02-28.95 wt% and 30.71-31.50 wt% were recorded
471 with 10 and 50°C/min heating rate respectively throughout the carrier gas flow range used in this
472 study.

473

474 **Figure 6:** Interaction graphs and the corresponding surface response plots for the combined
475 effects of process variables on non-condensable gas yield (a) and (b) effect of
476 nitrogen flow and temperature at 30°C/min; (c) and (d) effect of heating rate and
477 temperature at 15L/min N₂; (e) and (f) effect heating rate and nitrogen flow at 600°C

478

479 3.4 Optimization and validation of result

480 In order to maximize the bio-oil yield, the process variables considered in this study were
481 optimized. Pyrolysis temperature, heating rate, and nitrogen flow rate were maintained within the

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

492

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

494

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

496

497 The bio-oil yield from NGS observed at the optimized condition (600 °C, 5 L/min N₂ and 50
498 °C/min) in this study is similar to the liquid product reported by [Strezov et al. \(2008\)](#) during the
499 pyrolysis of NG. They observed 54.37 wt% bio-oil yield at 50 °C/min and 500 °C pyrolysis
500 temperature under argon atmosphere. Similarly, the result of pyrolysis study of NG by [De Conto
501 et al. \(2016\)](#) showed a total bio-oil yield of 52.99 wt% at 700 °C, 25 °C/min and 1 L/min nitrogen
502 flow. [Sousa et al. \(2016\)](#) also reported a total liquid product of 48.2 wt% from the pyrolysis of
503 NGS at 540°C. Report by [Lee et al. \(2010\)](#) on NG pyrolysis showed a lower oil yield of 36 wt%
504 at 500 °C and 150 °C/min higher heating rate under nitrogen atmosphere. These variations in the

505 yield of bio-oil from NG biomass can be linked to the characteristic of the feedstock used,
506 heating and heat transfer rates of the reactor, and the difference in the pyrolysis condition
507 (temperature, inert gas flow).

508 *3.5 Physicochemical properties of bio-oil produced at optimized condition*

509 The bio-oil product collected throughout this study was two-phase liquid, the organic phase (high
510 molecular weight component) and aqueous phase (low molecular weight component). The
511 organic fractions are usually water-insoluble derived from lignin component of the feed biomass
512 while the light fractions consist predominantly water (originates from both moisture in the feed
513 biomass and pyrolysis reaction), acids, ketones, aldehydes, small fraction of phenols and other
514 water-soluble organics (Resende et al., 2015). The physicochemical characteristics of the oil
515 produced at optimized condition are summarized in Table 7. Both the organic and aqueous
516 phases present an acidic characteristics with corresponding pH values of 3.71 and 2.09. This
517 property is attributed to presence of organic acids and phenolics in the bio-oil. The presence of
518 water in the pyrolysis oil is mainly from moisture in the feed biomass and product of dehydration
519 during the pyrolysis reaction (Resende et al., 2015; Mohammed et al., 2015b). In this study, the
520 biomass feedstock used was bone dry and, therefore, the water content of the oil could be said to
521 have originated from the pyrolysis reaction. Despite a careful separation of the aqueous phase,
522 7.24 wt% water remained in the organic phase. Solid content of the organic phase was
523 determined as ethanol insoluble. Bio-oil concentration of 1.25 wt% (1 g of bio-oil sample in 80 g
524 of ethanol) was used. The mixture was agitated and then filtered using 0.1µm filter. The filter
525 and retentates was thereafter oven dried at 105 °C for 30 min. Total solid content of less than
526 0.01 wt% (0.008-0.009) was recorded. Other characteristics of the organic phase such as density,
527 viscosity, ash content and calorific value reasonably conform to the ASTM specifications for

528 pyrolysis oil. Consequently, the organic phase bio-oil from NGS can be regarded as ASTM-
529 Grade D bio-oil. Carbon and oxygen contents from the ultimate analysis revealed that the
530 organic phase bio-oil has higher carbon (51.14 wt%) and lower oxygen (41.66 wt%) compared to
531 the value reported by Lee et al. (2010) (6.04 wt%-carbon); Sousa et al. (2016) (41.85 wt%-
532 carbon). High carbon content in the organic phase connotes presence carbon-rich organic
533 molecules which have resulted in the higher heating value (HHV) of 26.42 MJ/kg.

534
535

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

537

538 3.6 *Fourier-transform infra-red (FTIR)*

539 FTIR spectra of chemical species in the bio-oil samples are shown in Figure 7 (a & b). The
540 common broad peak around 3439 cm^{-1} implies that the samples contain chemical compounds
541 with hydroxyl group (O–H) such as water, alcohols and phenol (Guo et al., 2015; Bordoloi et
542 al., 2015). The peak at a frequency around 2970 cm^{-1} is due C–H stretching vibration which is
543 present only in the Figure 6b indicating the presence of saturated hydrocarbon in the organic
544 phase while the peak at a frequency around 2100 cm^{-1} common to both phases is ascribed to the
545 $\text{C}\equiv\text{C}$ functional group (Guo et al., 2015; Bordoloi et al., 2015). Vibration observed between
546 1625 cm^{-1} and 1707 cm^{-1} in both oil phases is attributed to $\text{C}=\text{O}$ which signifies the presence
547 of aldehydes, ketones or carboxylic acids. The vibration around 1462 cm^{-1} present in the organic
548 phase is ascribed $\text{C}=\text{H}$ indicating the presence of alkenes/aromatic hydrocarbons while the
549 peak between 1388 and 1364 cm^{-1} in both cases is due to $\text{C}-\text{H}$ bond (Yorgun and Yildz, 2015).
550 The sharp band around 1221 , 1269 , 1016 and 1092 cm^{-1} are due to $\text{C}-\text{O}$ vibration indicating the
551 presence of alcohol and esters. The fingerprint between 900 and 620 cm^{-1} are ascribed to
552 aromatic $\text{C}-\text{H}$ bending vibrations (Pan et al. 2012).

553

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

556

557

558

559 3.7 TGA of the organic phase bio-oil

560 Thermogravimetric analysis of bio-oil provides data on weight loss by evaporation as sample is
561 heated over a certain temperature range. The resulting information similar to the distillation data,
562 which can be used to estimate amount of bio-oil that will distill into specific fuel products. In this
563 study, TGA analysis of commercial fossil premium motor spirit (PMS), kerosene and diesel was
564 performed as standard. The organic bio-oil was subjected to the same thermal treatment. From
565 Figure 8 (a), final evaporation temperature of PMS, kerosene and diesel was found to be 126,
566 185 and 291 °C respectively. Using the final evaporation temperature, by extrapolation, the
567 organic phase bio-oil constitutes (Figure 8b) about 70wt% volatile fraction. The mass loss above
568 300 °C can be attributed to thermal decomposition of the residue. About 68 wt% of the oil has
569 boiling range similar to that of diesel. Similarly, approximately 53 wt% of the bio-oil is made up
570 of kerosene boiling fraction while 35 wt% has boiling characteristic comparable to that of PMS.
571 Also, information from the TGA simulated distillation can also be used as an indicator for
572 selecting temperature condition for GC-MS analysis of the oil. Based on the injection
573 temperature selected (250 °C) for the bio-oil characterization, only about 62 % of the oil can be
574 analyzed by the GC-MS.

575 3.8 GC-MS analysis of the organic phase bio-oil

576 Identification of detail chemical compounds in the bio-oil samples was carried out by GC-MS.
577 Library search of twenty (20) most abundant compounds using MS NIST library 2011 showed
578 that the organic phase (Table 8a) consists predominantly benzene derivatives such as phenols,
579 methyl-phenol, ethyl-phenol, methoxy-phenols, methoxy-benzene, benzaldehyde and benzene
580 carboxylic acid, which constitute accounted for about 60 % of the total organic phase, which is in
581 strong agreement with the bio-oil composition reported by [Lim et al \(2016\)](#). Other compounds
582 identified are hydrocarbons (dimethylcyclohexene and ethylbiphenyl). These together can be
583 processed to fuels and valuable chemicals. The aqueous phase (Table 8b) comprised mainly
584 organic acids, esters, ketones, aldehydes and oxygenated aromatics. The composition of organic
585 phase bio-oil in this study is similar to the result of GC-MS analysis reported by [Strezov et al.](#)
586 [\(2008\)](#). The oil analyzed by the author consisted large amount of benzene derivatives (24.46
587 wt%). The composition of bio-oil reported by [Lee et al. \(2010\)](#) was made up of 27.2 % organic
588 acids, 7.9 % phenols, which is comparable to the aqueous phase composition in this study.
589 Generally, the bio-oil aqueous phase is considered less important and often discarded as paralysis
590 by-products due to lack of specific applications. However, recent studies have proposed
591 production of hydrogen *via* catalytic aqueous, and steam reforming processes from this stream
592 ([Resende et al., 2015](#); [Chan et al., 2015](#)).

593

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

596

597 3.9 GC analysis of the non-condensable gas

598 Samples of non-condensable gas were collected at different temperature (450, 600 and 750 °C)
599 under the pyrolysis condition of 50 °C/min and 5 L/min N₂ as shown in Figure 9. The gas
600 composition (nitrogen free basis) detected include hydrogen (H₂), carbon monoxide (CO),
601 carbon dioxide (CO₂) and methane (CH₄). At 450 °C, the main components of the gas were CO₂
602 (16.42 vol%), H₂ (15.44 vol%) and CO (9.79 vol%). The high amount of CO₂ and H₂ and the
603 release of CO are attributed to fragmentation and subsequent transformation of unstable carbonyl
604 and carboxyl groups from depolymerization of holocellulose (hemicellulose and cellulose) and
605 the resulting char transformation (Collard and Blin, 2014). The trace of CH₄ (0.84 vol%)
606 detected at this temperature is mainly due to demethylation of char from hemicellulose and
607 fragmentation of methoxy group of lignin. As the temperature increased, the amount of CO₂
608 declined considerably due to the fact that fragmentation of glycosidic bonds in the holocellulose
609 must have been completed. This observation is in strong agreement with the TG/DTG result. A
610 total of 14.04 and 12.56 vol% CO₂ was recorded at 600 and 750 °C respectively. The amount of
611 CO₂ recorded at 450°C (16.42 vol%) in this study is similar to the value (18.5% CO₂) reported by
612 Strezov et al. (2008) during the pyrolysis of NG at 500 °C. Decline in the amount of CO₂ with
613 increasing pyrolysis temperature has been reported by De Conto et al. (2016). The authors
614 recorded CO₂ value of about 42.25 vol% at 500 °C, which declined substantially to around 12 vol
615 % at 600 °C and then to about 9.vol% at 700 °C. The continuous rise in the CO, H₂ and CH₄
616 components of the non-condensable gas with pyrolysis temperature can be ascribed to carbon-
617 carbon scission within the lignin and demethylation of final residue from the sample. This can
618 also be attributed to the pyrolysis secondary reactions usually promoted by mineral elements in
619 the biomass, particularly the alkali and alkali element (K, Ca) (Mohammed et al., 2016b). At 600

620 °C, the amount of H₂, CO and CH₄ recorded was 25.32, 13.60 and 3.36 vol% respectively. This
621 value increased to 35.45, 23.12 and 6.55 vol% correspondingly. The ratio of H₂/CO (vol%/vol%)
622 increased from 1.58 to 1.86 at 450 to 600 °C and there after decreased to 1.53 at 750 °C. This
623 indicate that the non-condensable gas from NG pyrolysis is a suitable feedstock for Fischer-
624 Tropsch (FT) synthesis, where the syngas can be further processed into liquid fuel (Pirola et al.,
625 2014; De Conto et al., 2016). However, presence of hydrogen sulfide (H₂S) in bio-syngas is a
626 common characteristic of a non-condensable gas from biomass pyrolysis due to the presence of
627 sulfur in the feedstock (Mohammed et al., 2015b). Catalyst used in the FT synthesis are highly
628 sensitive to H₂S even at part per million level (Yamamoto et al., 2015). Gas cleaning is therefore
629 need prior to the FT process. H₂S can be selectively removed from gas stream by absorption with
630 the aid of selexol solvent (Mohammed et al., 2014a).

631 3.10 Characteristics of produced bio-char

632 Physicochemical properties of NGS bio-char produced at different temperature and 50 °C/min
633 and 5 L/min nitrogen flow are summarized in Table 9. Volatile matter (VM) and heating value of
634 the bio-char decreased with increasing pyrolysis temperature while the ash content (AC) and
635 fixed carbon (FC) increased. This means that with increasing temperature, more VM is released
636 and highly thermal stable and non-volatile components of the source biomass are left within the
637 remaining solid. Reduction in the heating value is attributed to the increased AC, which is non-
638 combustible and generally has negative impact on the solid fuel (Mohammed et al., 2014b). The
639 ultimate analysis showed increased carbon content (C) with pyrolysis temperature while oxygen
640 (O), and hydrogen (H) decreased (Table 9). This can be attributed to structural transformation of
641 char via scission and cracking of weak bond within the bio-char structure. Similarly, nitrogen (N)
642 and sulfur (S) content also declined with pyrolysis temperature. This shows that N and S

643 compounds are released during pyrolysis (De Conto et al., 2016), which is responsible for the
644 sulfur and nitrogenous compounds detected in the bio-oil (Table 8).

645 Thermal stability of bio-char can be evaluated from the proximate, ultimate and TGA analyses.
646 De Conto et al. (2016) reported that the ratio of FC to the sum of FC and VM [$FC / (VM+FC)$] of
647 bio-char is an indicator of thermal stability. A ratio between 0.78 and 0.85 were recorded in this
648 study, which indicates high thermal stability of organic matter in the bio-char. Spokas (2010),
649 reported that there is connection between bio-char stability and O/C molar ratio. The author
650 stated that O/C ratio below 0.2 signifies a minimum bio-char half-life of 1000 years. In this
651 study, O/C mole ratio of 0.22, 0.15 and 0.09 was observed for the bio-char produced at 450, 600
652 and 750°C respectively. Similarly, Harvey et al. (2012) proposed a recalcitrance index (R_{50}) for
653 evaluating bio-char suitability for carbon sequestration. The authors defined R_{50} as the ratio of
654 temperature of bio-char ($T_{50 \text{ bio-char}}$) to temperature of graphite ($T_{50 \text{ graphite}}$) at which both materials
655 decompose 50% initial weight under oxygen atmosphere. They grouped bio-char based on the
656 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
657 C represent carbon sequestration potential similar to graphite, intermediate sequestration
658 potential and carbon sequestration potential similar to the biomass plant. Thermal decomposition
659 of the produced bio-char in oxygen atmosphere (50 mL/min) was carried out from ambient to
660 900 °C at 10 °C/min (Figure 10). Thermal stability increased with pyrolysis temperature.
661 Decomposition of the bio-char produced at pyrolysis temperature of 450, 600 and 750 °C
662 commenced at 250, 309 and 320 °C respectively. The corresponding $T_{50 \text{ bio-char}}$ was 380, 385 and
663 392 °C. Using 886 °C for $T_{50 \text{ graphite}}$ (Harvey et al., 2012), the equivalent R_{50} value was 0.43, 0.43
664 and 0.44. Hence, the bio-chars from NGS in this study are class C and have potential carbon
665 sequestration similar to the uncharred biomass plant. Also, the TGA result indicate that the char

666 can be used in processes under moderate temperature up to 300 °C. Residue (non-combustible)
667 from the TGA profile (Figure 10) increased with temperature pyrolysis temperature. This
668 observation is in good agreement with the proximate analysis results particular the increased ash
669 content observed with pyrolysis temperature.

670 Scanning electron micrograph and elemental mapping of the bio-char (Figure 11) showed that
671 the materials have porous structures, which increased with pyrolysis temperature. This result was
672 further confirmed using physisorption analysis. The specific surface area recorded for the bio-
673 char produced at 450, 600 and 750 °C was 0.014, 0.126 and 0.293 m²/g and the corresponding
674 pore volume of 0.08, 0.10 and 0.13cm³/g was observed. From elemental mapping of the bio-char
675 (Figure 11), potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P) and chlorine (Cl)
676 constitute the major mineral elements in the bio-char, which originated from the source biomass.
677 K, Ca, Mg and P are macronutrients needed for most plant growth. Bio-char can therefore be
678 applied as a source of macronutrient for agricultural production.

679 **4. Conclusions**

680 Pyrolysis of Napier grass was carried out in a vertical fixed bed tubular reactor. Optimization of
681 process variables such as temperature, heating rate and nitrogen flow rate was performed by
682 means of central composite design approach. The individual model equation for bio-oil, bio-char
683 and non-condensable gas yield was developed using set of experimental data and analysis of
684 variance. Temperature, nitrogen flow rate and heating rate had significant impact on the bio-oil
685 and non-condensable gas yield while the bio-char yield was mainly affected by the pyrolysis
686 temperature.. The oil yield was maximized by optimizing the process variables and optimum bio-
687 oil yield of 51.94 wt% was predicted at 600 °C, 50 °C/min and 5 L/min nitrogen flow. This result
688 was further validated through multiple experiments and the average value of the experimental

689 results was in good agreement with the predicted value. Therefore, it can be inferred that the
690 developed quadric model for bio-oil yield is adequate. The optimum bio-oil yield recorded in this
691 study is higher than the pyrolysis oil yield derived from Napier grass reported in the literature.
692 The bio-oil obtained throughout was two-phase liquid, the organic phase (high molecular weight
693 component) and aqueous phase (low molecular weight component). Both phases collected at
694 optimized condition were characterized using standard analytical techniques. The results
695 revealed that the organic phase consists mainly various benzene derivatives and hydrocarbons
696 which can be further processed into fuels and valuable chemicals while the aqueous phase was
697 predominantly water, acids, ketones, aldehydes and some phenolics and other water-soluble
698 organics. The non-condensable gas was made-up of methane, hydrogen, carbon monoxide and
699 carbon dioxide with high hydrogen/carbon monoxide ratio suitable for Fischer-Tropsch (FT)
700 synthesis. Biochar collected was a porous carbonaceous material, rich in mineral elements,
701 which may be used as adsorbent, solid fuel or source of macronutrient for agricultural
702 production. The bio-char also possessed potential for carbon sequestration. This study
703 demonstrated that Napier grass biomass is a potential feedstock for production of high-value
704 bioenergy precursors.

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