Sheffield Hallam University

Valorization of Napier grass via intermediate pyrolysis: Optimization using response surface methodology and pyrolysis products characterization

MOHAMMED, Isah Yakub, ABAKR, Yousif Abdalla, YUSUP, Suzana and KABIR, Feroz <http://orcid.org/0000-0002-3121-9086>

Available from Sheffield Hallam University Research Archive (SHURA) at:

http://shura.shu.ac.uk/14123/

This document is the author deposited version. You are advised to consult the publisher's version if you wish to cite from it.

Published version

Repository use policy

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

Isah Yakub Mohammed [1,5*]**, Yousif Abdalla Abakr** [2] **Suzana Yusup** [3] **and Feroz Kabir Kazi** [4]

[1]Department of Chemical and Environmental Engineering, the University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

[2]Department of Mechanical, Manufacturing and Material Engineering, the University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

[3]Department of Chemical Engineering, Universiti Teknology Petronas (UTP), Bandar Seri Iskandar, Tronoh 31750, Malaysia

[4]Department of Engineering and Mathematics, Sheffield Hallam University, City Campus, Howard Street, Sheffield S1 1WB, UK

[5]Crops for the Future (CFF), the University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

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 ^{o}C, 50 ^{o}C/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

*Corresponding author: Isah Yakub Mohammed (kebx3iye@nottingham.edu.my)

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

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 ^{o}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 ^{o}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 ^{o}C/min) on the pyrolysis product distribution. In each case, the system was ramped to a

108 maximum temperature of 900 ^{o}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 ^{o}C/min promoted the formation of smaller

111 acids and benzene fractions in the bio-oil compared to the low heating rate of 10 ^{o}C/min. CO_2

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 ^{o}C/min and biomass particle size within 2 mm at pyrolysis temperature of 500 ^{o}C. Their

119 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

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 ^{o}C was made up of high hydrogen

150 (H_2)/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 ^{o}C and heating rate of 10 ^{o}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 ^{o}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 ^{o}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 ^{o}C), nitrogen flow rate (5-25 L/min) and

195   heating rate (10-50 ^{o}C/min) were selected in this study.

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

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

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

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

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.

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

222

223   Where Y is the predicted response, n is the number of experiments, β_o, 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 0.25µm) (PerkinElmer-Elite^{TM}-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 programed at 60 ^{o}C, 80 ^{o}C and

258 200 ^{o}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 ^{o}C/min from ambient temperature to 100 ^{o}C and held

295   there for 30min to eliminate all the physically absorbed moisture and thereafter, ramped to 900

296 ^{o}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 ^{o}C, 229-285 ^{o}C, 326 ^{o}C and 373-540 ^{o}C. Visible peak at about 200 ^{o}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 ^{o}C and is ascribed

309 to the fast decomposition of hemicellulose as a result of cleavage of the glyosidic 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 ^{o}C.

313 This is attributed to cellulose decomposition and had a maximum weight loss of 35.74 wt%.

314 Temperature between 373 and 540 ^{o}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 ^{o}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

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

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, A^2, 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 A^2>A>C>AC>B>AB while the quadratic terms B^2, C^2 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 A^2

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, A^2, AB, AC, with A being the

353 most significant term having F-value of 557.41 (Table 4c). The coefficient of determination, R^2

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 (R^2) in relation to the sample size and the model terms,

357 and the corresponding value is 0.9878, 0.9861 and 0.8903. The R^2 and adjusted R^2 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 R^2 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.

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°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

409   at the higher heating rate. (Yorgun and Yildz, 2015). The oil yield decreased to 37.10 wt% at

410   both heating rates under the same temperature (750 ^{o}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 ^{o}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 ^{o}C/min heating

414   rate remained higher compared to the oil collected at 10 ^{o}C/min but no significant impact of

415   nitrogen flow was observed in both cases. Bio-oil yield at 50 ^{o}C/min was between 50.72 and

416   51.94 wt% relative to 46.45-48.03 wt% oil recorded at 10 ^{o}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 N$_2$; (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   ^{o}C/min and 50 ^{o}C/min throughout the investigated temperature range. Bio-char yields recorded

433   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

434   ^{o}C/min and 50 ^{o}C/min heating rate respectively. The slightly lower value of bio-char recorded at

435   50 ^{o}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 ^{o}C/min remained the same (around 20 wt %) while between 20.48 to 22.84

439   wt% char yield was recorded at 10 ^{o}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 Yildz, 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 N$_2$; (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 ^{o}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 ^{o}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 ^{o}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 ^{o}C, the non-condensable gas yield increased from 26.46 to 42.94 wt% and 20.62 to 43.55 wt% at

465 10 ^{o}C/min and 50 ^{o}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 Yildz, 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 N$_2$; (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 ^{o}C, 5 L/min nitrogen flow

486 rate, and 50 ^{o}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 ^{o}C, 5 L/min N_2 and 50

498 ^{o}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 ^{o}C/min and 500 ^{o}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 ^{o}C, 25 ^{o}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 ^{o}C and 150 ^{o}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 ^{o}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 $C \equiv C$ 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 $C = O$ 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 $C = H$ indicating the presence of alkenes/aromatic hydrocarbons while the

549 peak between 1388 and 1364 cm^{-1} in both cases is due to $C-H$ bond (Yorgun and Yildz, 2015).

550 The sharp band around 1221, 1269, 1016 and 1092 cm^{-1} are due to $C-O$ vibration indicating the

551 presence of alcohol and esters. The fingerprint between 900 and 620 cm^{-1} are ascribed to

552 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.

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 ^{o}C)

599   under the pyrolysis condition of 50 ^{o}C/min and 5 L/min N_2 as shown in Figure 9. The gas

600   composition (nitrogen free basis) detected include hydrogen (H_2), carbon monoxide (CO),

601   carbon dioxide (CO_2) and methane (CH_4). At 450 ^{o}C, the main components of the gas were CO_2

602   (16.42 vol%), H_2 (15.44 vol%) and CO (9.79 vol%). The high amount of CO_2 and H_2 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 CH_4 (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 CO_2

608   declined considerably due to the fact that fragmentation of glyosidic 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% CO_2 was recorded at 600 and 750 ^{o}C respectively. The amount of

611   CO_2 recorded at 450°C (16.42 vol%) in this study is similar to the value (18.5% CO_2) reported by

612   Strezov et al. (2008) during the pyrolysis of NG at 500 ^{o}C. Decline in the amount of CO_2 with

613   increasing pyrolysis temperature has been reported by De Conto et al. (2016). The authors

614   recorded CO_2 value of about 42.25 vol% at 500 ^{o}C, which declined substantially to around 12 vol

615   % at 600 ^{o}C and then to about 9.vol% at 700 ^{o}C. The continuous rise in the CO, H_2 and CH_4

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 ^{o}C, the amount of H_2, CO and CH_4 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 H_2/CO (vol%/vol%)

622 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

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 (H_2S) 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 H_2S even at part per million level (Yamamoto et al., 2015). Gas cleaning is therefore

629 need prior to the FT process. H_2S 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 ^{o}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 ^{o}C at 10 ^{o}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 ^{o}C

662   commenced at 250, 309 and 320 ^{o}C respectively. The corresponding $T_{50 \text{ bio-char}}$ was 380, 385 and

663   392 ^{o}C. Using 886 ^{o}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 $^{\circ}$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 $^{\circ}$C was 0.014, 0.126 and 0.293 m^2/g and the corresponding

674 pore volume of 0.08, 010 and 0.13cm^3/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 $^{\circ}$C, 50 $^{\circ}$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.

708

709

710

711

712

713

714

715

716

References

Anca-Couce, A., 2016. Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis. Progress in Energy and Combustion Science 53, 41-79

Bordoloi, N., Narzari, R., Chutia, R.S., Bhaskar, T., Kataki, R., 2015. Pyrolysis of Mesua ferrea and Pongamia glabra seed cover: Characterization of bio-oil and its sub-fractions. Bioresource Technology 178, 83–89

Braga, R.M., Melo, D.M.A., Aquino, F.M., Freitas, J.C.O., Melo, M.A.F., Barros, J.M.F., 2014. Characterization and comparative study of pyrolysis kinetics of the rice husk and the elephant grass. Journal of Thermal Analysis and Calorimetry. 115(2), 1915–1920

Bridgwater, A.V., 2012. Review of Fast Pyrolysis of biomass and product upgrading. Biomass Bioenergy 38, 68–94.

Brosse, N., Dufour, A., Meng, X., Sun, Q., Ragauskas, A., 2012. Miscanthus: a fast-growing crop for biofuels and chemicals production. Biofuels, Bioproducts and Biorefining 6, 580–598

Cadoux, S., Riche, A.B., Yates, N. E., Machet, J-M., 2012. Nutrient requirements of Miscanthus x giganteus: Conclusions from a review of published studies. Biomass and Bioenergy 38, 14-22

Caputo, A., 2014. Trends in European bioenergy law: problems, perspectives and risks. Journal of Culture, Politics and Innovation 2014 (1-2), 1-24.

Carraretto, C., Macor, A., Mirandola, A., Stoppato, A., Tonon, S., 2004. Biodiesel as alternative fuel: experimental analysis and energetic evaluations. Energy 29, 2195–2211.

Chaiwat, W., Gunawan, R., Gholizadeh, M., Li, X., Lievens, C., Hu, X., Wang, Y., Mourant, D., Rossiter, A., Bromly, J., Li, C-Z., 2013. Upgrading of bio-oil into advanced biofuels and chemicals. Part II. Importance of holdup of heavy species during the hydrotreatment of bio-oil in a continuous packed-bed catalytic reactor. Fuel 112, 302–310

Chen, A., Pan, C., Cao, D., Lou, H., 2015. Aqueous-phase reforming of the low-boiling fraction of bio-oil for hydrogen production: The size effect of Pt/Al_2O_3. International Journal of Hydrogen Energy 40(43), 14798–14805

Cherubini, F., 2010. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management 51, 1412–21.

747   Collard, F.X., Blin, J., 2014. A review on pyrolysis of biomass constituents: Mechanisms and
748   composition of the products obtained from the conversion of cellulose, hemicelluloses and
749   lignin. Renewable and Sustainable Energy Reviews 38, 594–608

750   De Conto, D., Silvestre, W.P., Baldasso, C., Godinho, M., 2016. Performance of Rotary Kiln
751   Reactor for the Elephant Grass Pyrolysis. Bioresource Technology 218, 153-160

752   Eom, I.Y., Kim, J.Y., Lee, S.M., Cho, T.S., Yeo, H., Choi, J.W., 2012. Comparison of pyrolytic
753   products produced from inorganic-rich and demineralized rice straw (Oryzasativa L.) by
754   fluidized bed pyrolyzer for future biorefinery approach. Bioresource. Technology. 128,
755   664–672

756   Flores, R. A., Urquiaga, S., Alves, B.J.R., Collier, L.S., Boddey, R. M., 2012. Yield and quality
757   of elephant grass biomass produced in the cerrados region for bioenergy. Engenharia
758   Agrícola 32(5), 831-839.

759   Gómez, N., Rosas, J.G., Cara, J., Martínez, O., Alburquerque, J.A., Sánchez, M.E., 2016. Slow
760   pyrolysis of relevant biomasses in the Mediterranean basin. Part 1. Effect of temperature on
761   process performance on a pilot scale. Journal of Cleaner Production 120, 181-190.

762   Guo, Y., Song, W., Lu, J., Ma, Q., Xu, D., Wang, S., 2015. Hydrothermal liquefaction of
763   Cyanophyta: Evaluation of potential bio-crude oil production and component analysis.
764   Algal Research 11, 242–247

765   Harvey, O.R., Kuo, L.J., Zimmerman, A.R., Louchouarn, P., Amonette, J.E., Herbert, B.E.,
766   2012. An index-based approach to assessing recalcitrance and soil carbon sequestration
767   potential of engineered black carbons (Biochars). Environmental Science and Technology
768   46 (3), 1415–1421

769   Heidenreich, S., Foscolo, P. U., 2015. New concepts in biomass gasification. Progress in Energy
770   and Combustion Science 46, 72-95

771   Imam,T., Capareda, S., 2012. Characterization of bio-oil, syn-gas and bio-char from switchgrass
772   pyrolysis at various temperatures. Journal of Analytical and Applied Pyrolysis 93, 170-177

773   Kan, T., Strezov, V., Evans, T.J., 2016. Lignocellulosic biomass pyrolysis: A review of product
774   properties and effects of pyrolysis parameters. Renewable and Sustainable Energy Reviews
775   57, 1126–1140

776   Lee, M.-K., Tsai, W.-T., Tsaic, Y.-L., Lin, S.-H., 2010. Pyrolysis of Napier grass in an
777   induction-heating reactor. Journal of Analytical and Applied Pyrolysis 88, 110–116.

778   Lim, C.H., Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S. and Lam, H.L., 2016. Novel
779   input-output prediction approach for biomass pyrolysis. Journal of Cleaner Production, 30,
780   1-11.

781 Lim, C.H., Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S. and Lam, H.L., 2015. Element
782   characteristic tolerance for semi-batch fixed bed biomass pyrolysis. Chemical Engineering
783   Transactions 45, 1285-1290

784 .

785 Mohammed, I. Y., Samah, M., Mohamed, A., & Sabina, G. 2014a. Comparison of SelexolTM
786   and Rectisol® Technologies in an Integrated Gasification Combined Cycle (IGCC) Plant
787   for Clean Energy Production. International Journal of Engineering Research 3(12), 742-
788   744

789 Mohammed, I.Y., Abakr, Y.A., Kazi, F.K. and Yusuf, S., 2016a.. Effects of pretreatments of
790   Napier grass with deionized water, sulfuric acid and sodium hydroxide on pyrolysis oil
791   characteristics. Waste and Biomass Valorization, 1-19.

792 Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S., Alshareef, I., Chin, S.A., 2015b. Pyrolysis
793   of Napier Grass in a Fixed Bed Reactor: Effect of Operating Conditions on Product Yields
794   and   Characteristics.   BioResources
795   10 (4), 6457–6478.

796 Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S., Alshareef, I., Chin, S.A., 2015a.
797   Comprehensive Characterization of Napier Grass as a Feedstock for Thermochemical
798   Conversion. Energies 8(5), 3403-3417.

799 Mohammed, I.Y., Kazi, F.K., Yusuf, S.B., Alshareef, I. and Chi, S.A., 2014b. Higher Heating
800   Values (HHV) Prediction Model from Biomass Proximate Analysis Data. In International
801   conference & exhibition on clean energy, October 20–22, Quebec, Canada.

802 Mohammed, I. Y., Abakr, Y. A., Musa, M., Yusup, S., Singh, A., & Kazi, F. K. (2016c).
803   Valorization of Bambara groundnut shell via intermediate pyrolysis: Products distribution
804   and characterization. Journal of Cleaner Production, 717-728.

805 Mohammed, I.Y., Kazi, F.K., Yusup, S., Alaba, P.A., Sani, Y.M., Abakr, Y.A., 2016d. Catalytic
806   Intermediate Pyrolysis of Napier Grass in a Fixed Bed Reactor with ZSM-5, HZSM-5 and
807   Zinc-Exchanged Zeolite-A as the Catalyst" Energies 9 (4), 246.

808 Mohammed, I.Y., Lim, C.H., Kazi, F.K., Yusup, S., Lam, H.L. and Abakr, Y.A., 2016b. Co-
809   pyrolysis of Rice Husk with Underutilized Biomass Species: A Sustainable Route for
810   Production of Precursors for Fuels and Valuable Chemicals. Waste and Biomass
811   Valorization, 1-11.

812 Ning, S-K., Hung, M-C., Chang, Y-H., Wan, H-P., Lee, H-T., Shih, R-F., 2013. Benefit
813   assessment of cost, energy, and environment for biomass pyrolysis oil. Journal of Cleaner
814   Production 59, 141-149

815   Pan, C., Chen, A., Liu, Z., Chen, P., Lou, H., Zheng, X., 2012. Aqueous-phase reforming of the
816   low-boiling fraction of rice husk pyrolyzed bio-oil in the presence of platinum catalyst for
817   hydrogen production. Bioresource Technology 125, 335–339

818   Patwardhan, P.R., Brown, R.C., Shanks, B.H., 2011. Product distribution from the fast pyrolysis
819   of hemicellulose. ChemSusChem 4(5), 636–643.

820   Pirola, C., Fronzo, A., Galli, F., Bianchi, C.L., Comazzi, A., Manenti, F., 2014. Biosyngas
821   Conversion by Fischer – Tropsch Synthesis: Experimental Results and Multi-scale
822   Simulation of a PBR with High Fe Loaded Supported Catalysts. Chemical. Engineering.
823   Transaction 37, 595-600.

824   Resende, K.A., Ávila-Neto, C.N., Rabelo-Neto, R.C., Noronha, F.B., Hori, C.E., 2015.
825   Thermodynamic analysis and reaction routes of steam reforming of bio-oil aqueous
826   fraction. Renewable. Energy 80,166–176.

827   Richter, G.M., Riche, A.B., Dailey, A.G., Gezan, S.A., Powlson, D.S., 2008. Is UK biofuel
828   supply from Miscanthus water-limited? Soil Use Manage 24, 235–245.

829   Samson, R., Mani, S., Boddey, R., 2005. The potential of C4 perennial grasses for developing a
830   global bioheat industry. Critical Reviews in Plant Sciences 24(5-6), 461–495.

831   Soetardji, J.P., Widjaja, C., Djojorahardjo, Y., Soetaredjo, F.E., Ismadjia, S., 2014. Bio-oil from
832   jackfruit peel waste. Procedia Chemistry 9,158 – 164.

833   Sousa, J.F., Bezerra, M.B.D., Almeida, M.B.B., Moure, G.T., Mesa-Perez, J.M., Caramao, E.B.,
834   2016. Characteristics of Bio-oil from the Fast Pyrolysis of Elephant Grass (Pennisetum
835   purpureum Schumach) in a Fluidized Bed Reactor. American Chemical Science Journal
836   14(2), 1-10

837   Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar
838   ratios. Carbon Management 1(2), 289–303

839   Strezov, V., Evans, T.J., Hayman, C., 2008. Thermal conversion of elephant grass (Pennisetum
840   Purpureum Schum) to bio-gas, bio-oil and charcoal. Bioresource Technology 99, 8394–
841   8399.

842   Tripathi, M., Sahu, J.N., Ganesan, P., 2016. Effect of process parameters on production of
843   biochar from biomass waste through pyrolysis: A review. Renewable and Sustainable
844   Energy Reviews 55, 467–481.

845   Tsai, W.T. and Tsai, Y.L., 2016. Thermochemical characterization of Napier grass as an energy
846   source and its environmental and economic benefit analysis. Energy Sources, Part B:
847   Economics, Planning, and Policy 11(2), 130-136.

848 Van de Velden, M., Baeyens, J., Brems, A., Janssens, B., Dewil, R., 2010. Fundamentals,
849   kinetics and endothermicity of the biomass pyrolysis reaction. Renewable Energy 35, 232–
850   242.

851 Yamamoto, T., Tayakout-Fayolle, M., Geantet, C., 2015. Gas-phase removal of hydrogen
852   sulfide using iron oxyhydroxide at low temperature: Measurement of breakthrough
853   curve and modeling of sulfidation mechanism. Chemical Engineering Journal 262, 702–
854   709.

855 Yorgun, S., Yıldız, D., 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters
856   on product yields and bio-oil characterization. Journal of Analytical and Applied Pyrolysis
857   114, 68–78

858 Zhou, Y., Jiang, J., Peng, Z., Wang, Q., Xiong, D., 2012. Ecosystem Management in the Natural
859   Rubber Industry. Journal of Resources and Ecology 3(3), 230-235

860 **Standards used**

861 BS EN 14774-1. Solid Biofuels. Determination of Moisture Content. Oven Dry Method. Total
862   Moisture. British Standards Institution 2009, London, UK
863 BS EN 15148. Solid biofuels. Determination of the content of volatile matter. British Standards
864   Institution 2009, London, UK

865 BS EN 14775. Solid biofuels. Determination of ash content. British Standards Institution 2009,
866   London, UK

867 BS EN 15290. Solid biofuels. Determination of major elements-Al, Ca, Fe, Mg, P, K, Si, Na and
868   Ti. British Standards Institution 2011, London, UK

869 BS EN 14918. Solid biofuels. Determination of calorific value. British Standards Institution
870   2009, London, UK

871 Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker, D. Determination of
872   Structural Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure.
873   National Renewable Laboratory 2012; NREL/TP-510-42618

874 20. ASTM D240. Standard test method for heat of combustion of liquid hydrocarbon fuels by
875   bomb calorimeter. ASTM International 2009, West Conshohocken, PA.
876 ASTM D7544 - 12 Standard Specification for Pyrolysis Liquid Biofuel. ASTM International
877   2012, West Conshohocken, PA.

878

879