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Effects of Pretreatments of Napier Grass with Deionized Water, Sulfuric Acid and Sodium Hydroxide on Pyrolysis Oil Characteristics

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Abstract

The depletion of fossil fuel reserves has led to increasing interest in liquid bio-fuel from renewable biomass. Biomass is a complex organic material consisting of different degrees of cellulose, hemicellulose, lignin, extractives and minerals. Some of the mineral elements tend to retard conversions, yield and selectivity during pyrolysis processing. This study is focused on the extraction of mineral retardants from Napier grass using deionized water, dilute sodium hydroxide and sulfuric acid and subsequent pyrolysis in a fixed bed reactor. The raw biomass was characterized before and after each pretreatment following standard procedure. Pyrolysis study was conducted in a fixed bed reactor at 600°C, 30°C/min and 30ml/min N_2 flow. Pyrolysis oil (bio-oil) collected was analyzed using standard analytic techniques. The bio-oil yield and characteristics from each pretreated sample were compared with oil from the non-pretreated sample. Bio-oil yield from the raw sample was 32.06 wt% compared to 38.71, 33.28 and 29.27wt% oil yield recorded from the sample pretreated with sulfuric acid, deionized water and sodium hydroxide respectively. GC-MS analysis of the oil samples revealed that the oil from all the pretreated biomass had more value added chemicals and less ketones and aldehydes. Pretreatment with neutral solvent generated valuable leachate, showed significant impact on the ash extraction, pyrolysis oil yield, and its composition and therefore can be regarded as more appropriate for thermochemical conversion of Napier grass.

Keywords: Napier grass; Ash; Pretreatment; Extractives; Pyrolysis; Bio-oil; Characterization

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1. Introduction

Fossil fuel remains the main source of energy supply globally despite the environmental impacts cum sociopolitical concerns which are well documented in the literature [1-4]. The fear of energy insecurity in the near future in addition to the need for reduction of greenhouse gases has led to the development of energy from alternative renewable sources such biomass, wind, solar and mini-hydro [5-8]. Among these renewable resources, biomass is the only renewable resource that has carbon in its building blocks which can be processed to liquid fuel. Lignocellulosic biomass (non-food materials) such as forest residues, agro-wastes, energy grasses, aquatic plants and algae etc have been seen as ideal raw materials in this direction as they have eliminated initial public perception of food insecurity associated with first generation biofuels which were produced from food materials [9, 10]. In addition, they have low level of sulfur and nitrogen contents which make them relatively environmental friendly. Napier grass (*Pennisetum purpureum*) is one of the perennial grasses with potentials of high biomass yield typically in the range of 25-35 oven dry tons per hectare annually which correspond to 100 barrels of oil energy equivalent per hectare compared to other herbaceous plants [11, 12]. Other advantages of Napier grass include compatibility with conventional farming practices, it outcompete weeds, need very little or no supplementary nutrients and therefore require lower establishment cost. It can be harvested up to four times within a year with a ratio of energy output to energy input of around 25:1 which makes it one of the most potential energy crops for development of efficient and economic bioenergy systems [11, 12].

Abbreviations

AAK	Acids, aldehydes and ketones
ACL	Acid leachate
ACTNGS	Acid treated Napier grass stem
ALL	Alkaline leachate
ALTNGS	Alkaline treated Napier grass stem
ASTM	American Society for Testing and Materials
BSI	British Standards Institution
C	Carbon (%)
c	Cellulose
CFF	Crops For the Future
DTG	Derivative of thermogravimetric
e	Extractives
EN	European Standard
EOS	Esters and other organic compounds
FTIR	Fourier transform infrared
GCMS	Gas chromatograph mass spectrometer
H	Hydrogen (%)
h	Hemicellulose
HC	Hydrocarbon
HHV	Higher heating value (MJ/kg)
l	Lignin
L/S	Liquid-solid ratio (wt/wt)
N	Nitrogen (%)
NGS	Napier Grass Stem
NIST	National Institute of Standards and Technology
NS	Nitrogenous and sulfur containing compounds
O	Oxygen (%)
RNGS	Raw Napier grass stem
Ro	Severity factor
rpm	Revolution per minute (min^{-1})
S	Sulfur (%)
TGA	Thermogravimetric analyzer

VAC	Value added chemicals
WL	Water leachate
WTNGS	Water treated Napier grass stem
$Y_{bio\text{-}char}$	Bio-char yield
$Y_{bio\text{-}oil}$	Bio-oil yield
YE	Energy yield (%)
YM	Mass yield (%)
$Y_{Noncondensable}$	Noncondensable yield

Biomass generally is a complex organic material consisting of different degrees of cellulose, hemicellulose, lignin, extractives and minerals. The minerals constitute the ash forming elements which are inorganic in nature. They originate either directly from the fuel or incorporated during fuel handling and cannot be used as energy [13, 14]. During biomass conversion especially in thermochemical process like pyrolysis, these materials tend to retard conversions, yield and selectivity by promoting side reactions which lead to the formation of unwanted products [15, 16]. In addition, they also have high tendencies of causing operational challenges such as fouling, erosion, slagging and corrosion [17, 18]. Reduction of these inorganic components via a pretreatment step prior to the pyrolysis process will go a long way in improving the quality of the oil and life span of the equipment. There are several biomass pretreatment methods depending on the conversion route and the desired end product. For thermochemical conversion process,, hydrothermal, steam explosion, torrefaction and chemical pretreatments are the most commonly used [19, 20, 21]. Hydrothermal pretreatment is a non-catalytic aqueous pretreatment method which involves the use of water at moderate temperature as solvent. Biomass is subjected to cooking under pressure which enhances extraction of ash up to about 60-75% and sugars [22]. Process parameters include liquid to solid mass ratio of 15, temperature of 190^{o}C, 8-10 minutes residence time, agitation speed of 150rpm and reactor pressure of 180psi [20, 23]. Hydrothermal pretreatment can be regarded as cost effective as solvent cost is relatively very low and requires no post-treatment of effluent. In addition, leachate from this process may contain some amount of sugars from partial solubilization of hemicellulose which can be further processed to bioethanol via biochemical process. However, this method can be challenging in large scale operation since it requires large volume of solvent which will generate corresponding volume of effluent. Proper control of temperature is also needed to avoid formation of degradation products [23]. Steam explosion of biomass has been carried out by many researchers. This technique was used in the past to extract cellulose for the production of ethanol. It separates hemicellulose, cellulose and lignin component of biomass via mechano-chemical process which involves adiabatic expansion of water inside the pore of biomass tissue and auto hydrolysis of the cell components [21]. Temperature and pressure between 160-240^{o}C and 0.7-4.8MPa are normally used for few minutes reaction time [24, 25, 26, 27]. Recently, studies by Biswas *et al*. [21] on steam explosion of salix wood chips at temperature between 205-228^{o}C and 6-12min reaction time showed about 25% ash reduction in the biomass. Steam explosion is characterized with release of phenolic compounds from the disruption of lignin, an important component of bio-oil and generation of toxic compound such as organic acids (acetic acid, formic acid and livulinic acid). Acetic acids are released from the acetyl groups in the hemicellulosic fraction while formic acid and livulinic acids are generated from degradation of furfural. [23]. Torrefaction, on the other hand, is a mild pyrolysis process usually carried out in an inert environment at a temperature between 200 and 300^{o}C for a certain period of time. Pretreated sample from this approach is easier to handle, thereby making it less energy intensive. This technique is generally employed to improve the characteristics of a solid fuel relative to the original biomass for combustion and gasification applications [28].

Chemical pretreatment consists of those methods that use either alkali or mineral acid as solvent to effect changes in original state of biomass in order to improve pyrolysis reactions and product selectivity. Alkali pretreatment results in disruption of ester and glycosidic side bond which lead to cellulose swelling and fractional decrystalization, incomplete solvation of hemicellulose and structural alteration of lignin [29-33]. The process is mostly conducted with dilute solution of sodium hydroxide (NaOH), $Ca(OH)_2$, ammonium hydroxide (NH_4OH), etc at temperature between 60-90°C, 1-2%wt/wt liquid-solid ratio, 10-60 minutes retention time and pressure of about 1-3MPa [23, 29-33]. This approach cannot be considered suitable for a pyrolysis process since large portion lignin is removed which is an important component of the feedstock in the pyrolysis process. In addition, the cost of pretreatment appears to be high due to consumption of the alkaline solvent which may requires recovery, thus adding extra cost to the entire process. In acid system, dilute solution of mineral acid such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), *Phosphoric acid* (H_3PO_4) etc is generally employed to eliminate ash and hemicellulose [19, 33, 34]. In a typical acid pretreatment, acid concentration of 0.2-2.5%w/w and operating condition of temperature between 25 to 100°C and retention time from few minutes to hours under agitation is used [23]. Acid pretreatment releases leachate that is usually highly acid and requires neutralization [23, 35, 36]. Furthermore, acid can cause corrosion to equipment and therefore need corrosion resistant materials for construction which are general expensive [23]. Consequently, fundamental studies on pretreatment of biomass are still needed for significant positive impact on the thermochemical process.

Catalytic and non-catalytic aqueous pretreatments of Napier grass, product characterization and their impacts on pyrolysis products distribution has not been reported in the literature. The objective of this study was to carry out pretreatment of Napier grass biomass using deionized water, NaOH and H_2SO_4 prior to pyrolysis and their impacts on the pyrolysis oil yield and characteristics.

2. Experiment

2.1 Materials and Characterization

Fresh Napier was harvested in July 2015 at the Crops for the Future (CFF) field Research Centre Semenyih, Malaysia and the stem (NGS) chopped 6 to 8cm was collected same day and transported in plastic bags to research building of the University of Nottingham Malaysia campus. The materials were subsequently oven dried at 105^{o}C for 16hrs to a constant weight according to BS EN 14774-1 standard [37]. The dried materials were then shredded in a rotor beater mill Retsch^R to particle sizes between 0.2-2mm and stored in air tight plastic bags for further studies. Before any subsequent analysis, sample from the sample bag was oven dried overnight. The volatile matter and ash content on dry basis were determined according British standards BS EN 15148 [38] and BS EN 14775 [39] respectively. Fixed carbon was computed by subtracting the percentage compositions of ash and volatile matter from the bone dry sample mass. Higher heating value (HHV) was determined using oxygen bomb calorimeter Parr 6100 following BS EN 14918 [40]. Elemental compositions were determined using a Perkin Elmer 2400 Series II CHNS/O analyzer (Perkin Elmer Sdn Bhd, Selangor, Malaysia). The nature of chemical bonds in the biomass was evaluated by Fourier transform infrared spectroscopy (FTIR) on a PerkinElmer Spectrometer Spectrum RX1 instrument (Perkin Elmer Sdn Bhd, Selangor, Malaysia) using the potassium bromide (KBr) method. The translucent KBr disc (13 mm diameter) was made from homogenized 2 mg samples in 100 mg KBr using a CARVER press at 5.5 tons for 5 min. Spectra were recorded with the Spectrum V5.3.1 software within the wavenumber range of 400–4000 cm^{-1} at 32 scans and 4 cm^{-1} resolution on a PerkinElmer

Spectrometer Spectrum RX1 instrument. Biomass inorganic mineral was analyzed using atomic absorption spectrometer (AAS) Perkin Elmer analyst 400 (Perkin Elmer Sdn Bhd, Selangor, Malaysia) according to BS EN 15290 [41]. Thermogravimetric study was carried out in thermogravimetric simultaneous thermal analyzer (STA) 6000 (TGA) (Perkin Elmer Sdn Bhd, Selangor, Malaysia) in nitrogen atmosphere, flow rate 20mL/min at temperature between 300-1100K and heating rate of 10 K/min and the structural compositions were determined. About 10.0mg (particle size of 0.2mm) of sample was used.

2.2 Pretreatment

Pretreatment study was carried out with NaOH, H_2SO_4 and type 1 ultrapure water (resistivity: > 18MΩ-cm; TOC: < 10ppb) as solvents. 40g of Napier grass sample (0.2-2mm) was used in each experiment with liquid/solid ratio of 5%w/w under agitation speed of 100rpm. NaOH and H_2SO_4 processes were conducted at 70^{o}C and 1hour retention time. For the deionized water, the temperature between 25-30^{o}C was used and the retention time varied from 30minutes to 6hours. The corresponding pretreatment severity factor was computed according to Overend *et al*. [42] as presented in the equation (1) below. Pretreatment severity factor is a pseudo-first-order reaction model which combines the treatment temperature and retention time in one value and gives an approximate indication of the treatment conditions. At the end of reaction, the solid residue was separated from leachate using vacuum filtration with the aid of sartolon polyamide filter paper (0.45µm pore size). The residue was further washed with deionized water until the pH of water wash was around 7. The materials were then oven dry at 105^{o}C for 16hrs to a constant weight. Samples pretreated with the pure water, acid and alkaline are herein regarded as WTNGS, ACTNGS and ALTNGS respectively. Mass and energy yields were calculated according to equation (2) and (3) respectively. The materials were further analyzed according to the procedure outlined above under characterization. Surface characteristics of the raw and pretreated samples were analyzed using Scanning electron microscopy (SEM, FEI Quanta 400 FE-SEM).

$$R_O = t \times \exp\left[\frac{T - 100}{14.75}\right] \tag{1}$$

Where t is pretreatment time (minute), T is pretreatment temperature (^{o}C)

$$\text{Yield}_M\ (\%) = \left[\frac{\text{Pretreated weight(g)}}{\text{Initial weight (g)}}\right] \times 100 \tag{2}$$

$$\text{Yield}_E\ (\%) = \left[\frac{\text{HHV}_{\text{Pretreated}}\ (\text{MJ/kg})}{\text{HHV}_{\text{Initial}}\ (\text{MJ/kg})}\right] \times \text{Yield}_M \tag{3}$$

Leachate from each solvent was analyzed. The pH of leachate was recorded with WalkLAB microcomputer pH meter TI9000 (Trans Instruments, Singapore) and sugar content was determined in degree Brix (°Bx) using Anton Paar density and concentration meters (DMA 4500 M, USA). Summary of the pretreatment process flow diagram is shown in Figure 1.

Figure 1: Pretreatment process flow diagram. (RNGS) raw NGS, (WTNGS) water treated NGS, (ACTNGS) acid treated NGS, (ALTNGS) alkaline treated NGS, (WL) water leachate, (ACL) acid leachate and (ALL) alkaline leachate.

2.3 Pyrolysis and products characterization

Pyrolysis was carried out in a fixed bed reactor made from stainless steel (4cm diameter and length 10cm) at 600^{o}C and nitrogen flow rate of 30mL/min. This condition has been established in our previous study [43]. The reactor was placed at center of a stainless steel tubular furnace as shown in Figure 2. The furnace was heated electrically at heating rate of 30^{o}C/min. The reactor temperature was monitored with a K-type thermocouple connected to computer through data logger. 30g of Napier grass sample (oven dried, 0.2-2mm particle size) was used in the experiment. The reaction time was kept at 15min (±2min) or until no significant amount of non-condensable gas was observed. The pyrolysis vapor was condensed by passing through a condenser connected to a chiller at 4^{o}C and the oil was collected. The bio-oil, bio-char and non-condensable gas yield was computed according to equation (4), (5) and (6) respectively.

$$\text{Yield}_{\text{bio - oil}}(\text{wt\%}) = \frac{\text{weight of the bio - oil collected}}{\text{biomass}} \times 100 \tag{4}$$

$$\text{Yield}_{\text{bio - char}}(\text{wt\%}) = \frac{\text{weight of the bio - char collected}}{\text{biomass}} \times 100 \tag{5}$$

$$\text{Yield}_{\text{non - condensable}}(\text{wt\%}) = 100 - (\text{Y}_{\text{bio - oil}} + \text{Y}_{\text{bio - char}}) \tag{6}$$

Figure 2. Pyrolysis system with a fixed bed reactor

After each production bio-oil was characterized within 24 hours. Higher heating value was determined using oxygen bomb calorimeter Parr 6100 according to ASTM D240-09 [44, 45]. WalkLAB microcomputer pH meter TI9000 was used to determine the pH. Density and viscosity were determined using Anton Paar density meter DMA 4500 M and Brookfield DV-E viscometer respectively. Bio-oil water content was determined using Karl Fischer V20 volumetric titrator Mettler Toledo for water content according to ASTM E 203 [45, 46]. Elemental compositions of bio were determined using the procedure outlined above under the feedstock characterization. Chemical compositions of bio-oils were determined using PerkinElmer Clarus^{R} SQ 8 gas chromatograph-mass spectrometer (GC-MS) system with quadruple detector and PerkinElmer-Elite^{TM}-5ms column (30m x 0.25mm x 0.25μm). The oven was programmed at initial temperature of 40^{o}C, ramp at 5^{o}C/min to 280^{o}C and held there for 20min. The injection temperature, volume and split ratio was 250^{o}C, 1μL and 50:1 respectively. Helium was used as carrier gas at flow rate of 1mL/min. The bio-oil samples 10% in chloroform were prepared and used for the analysis. MS ion source at 250^{o}C with 70eV ionization energy was used. Peaks of the chromatogram were identified by comparing with standard spectra of compounds in the National Institute of Standards and Technology (NIST) library.

3. Results and Discussion

3.1 Ash removal, mass and energy yield

Improvement in the energy yield of pretreated NGS was observed with increasing pretreatment severity (Ro) from 0.4 to 2.7 (Figure 3) in neutral solvent. Mass yield decreased from 84.12 to 80.61% while the energy yield increased from 84.12 to 85.33% which account for about 1.21% rise. The rise in energy was attributed to the level ash extraction achieved during the pretreatment (Figure 4) while the reduction in mass yield was due to the removal of extractives and solubilization of some parts of the hemicellulose [47-49,]. Although the value of energy rise appeared to be less significant due to the loss in the mass yield. This suggests that mass loss has a great impact on the energy recovery no matter how well the ash extraction maybe. However, the mass loss was relatively low as more than 80% of the initial mass of the sample was recovered after the pretreatment. Ash extraction under this treatment condition ranges from 20 to 64.29% (Figure 4). For an efficient and effective pretreatment process, a compromise between the energy and mass yield, percentage ash extraction and most importantly, the duration of pretreatment is needed. In large scale process, a lower pretreatment time will facilitate several treatments per day which will in turn impact positively both in quantity and quality in bio-oil production. Furthermore, catalytic activities of biomass ash is said to have high impact on the bio-oil quality when the ash content of the source biomass is more than 1.0% [50]. Ro value around 0.9 which corresponds to an hour operation yielded more than 83% mass and 84% energy with ash extraction above 50%. This translates to about 0.87wt% ash (Table 2) in the pretreated NGS compared to the raw NGS with 1.75wt% ash. Therefore, Ro value of 0.9 can be regarded as optimum condition for pretreatment of NGS biomass using neutral solvent. Sample treated at this condition was used for further analysis.

The pretreatment of NGS with sulfuric acid (0.5 to 2.5w/w% concentration) results in decrease in mass yield from 82.78 to 79.18% with corresponding energy yield from 84.42 to 87.35% (Figure 3). The decline in the mass yield is attributed to high solubilization of extractives, hemicellulose while the rise in the energy yield was due to high improvement in the heating value of the pretreated sample [47-50] brought by the level of ash extraction recorded (Figure 4). Generally, among the components of lignocellulosic material, hemicellulose is prone to hydrolytic attack due to resistance to hydrogen bond formation by some of its component such as glucuronic acid and acetic acid [48]. Acid concentrations from 0.5 to 1.5w/w% (Figure 3) showed a sharp increase in energy yield from 85.06 to 87.17% and thereafter remain relatively stable. The mass yield under this condition was within 80%. Also, about 70% ash extraction was recorded which is equivalent to 0.53wt% ash (Table 2) in the pretreated sample. This certifies the ash requirement of below 1wt% for high yield and quality bio-oil production. Thus, NGS sample treated at 1.5w/w% acid concentration was further analyzed.

Figure 3. Mass and energy yield of pretreated samples. (YM) mass yield and (YE) energy yield

Figure 4. Effect of pretreatment solvents on ash removal and extractives from NGS.

Pretreatment using NaOH (0.5-2.5w/w%) showed more effect on both mass and energy yields with continuous decline from 71.20 to 53.38% and 67.50 to 49.04% respectively (Figure 3). The decrease in mass yield was as a result of high removal of lignin, extractives, and some hemicellulose and cellulose [29-33]. The ash removal (Figure 4) declined with increasing alkaline concentration which in turn in addition to lignin removal lower the higher heating values of the pretreated samples. The combine effect of this is responsible for the decrease in the energy yield. Alkaline pretreatment cannot be considered suitable for a pyrolysis process since large portion lignin is removed which is an important component of the feedstock in the pyrolysis process. In addition, lower ash extraction recorded throughout this process with pretreated samples having ash content more than 1wt% (Table 2) is an indication that the pyrolysis process will be affected by catalytic activity of the biomass ash which will eventually lead to a poor quality bio-oil [50]. For the purpose of comparison with other solvents (H_2O and H_2SO_4), sample pretreated with 1.5w/w% NaOH was further examined.

3.2 Mineral compositions

Mineral compositions of NGS for both raw and pretreated samples are summarized in Table 1. Potassium (K) constitutes the most abundant metal in the raw NGS compared to other metals such as sodium (Na), calcium (Ca), Aluminum (Al), iron (Fe) and silicon (Si). This could be attributed to the nature of treatment or fertilizer used during the cultivation of the Napier grass. Leaching of the individual element in the biomass varied with solvent. High removal of alkaline metals such as sodium (Na) and potassium (K) were recorded with neutral solvent which increased with pretreatment Ro. The corresponding removal efficiency recorded was 90% and 74% respectively. This suggests that considerable amount of the Na and K in the NGS are present in form of water soluble salts which are generally salt of chlorides, nitrates, carbonates and phosphates [50-52]. For other elements, slight declines were observed in calcium (Ca), aluminum (Al), iron (Fe) and silicon (Si) content after the treatment. The Ca, Al and Fe minerals can be said to be in cation form bound to reactive sites of the NGS biomass which can be removed substantially through ion exchange [50-52]. The small reduction in Si content suggest that NGS biomass is made up of two forms of silica, the amorphous silica which is normally deposited on the outer walls of epidermal cells and dissolved in water as $Si(OH)_4$. While the second type is Si physiologically bond to the plant tissue which cannot be removed by the neutral solvent [53, 54].

Pretreatment using H_2SO_4 demonstrated high removal of both water soluble and insoluble mineral components in the NGS. High amount of Na, K, Ca, Al and Fe were leached due to high acidity of the solvent. The removal efficiency recorded under this treatment condition was 96, 95, 75, 52 and 56.97% for Na, K, Ca, Al and Fe. Generally, leaching with dilute acids removes soluble metals that are not physiologically bound to the plant tissue [50] and similar trends have been reported in the literatures [47-52]. On the other hand, NaOH pretreatment effectively removed Si and Al with 87% and 78% removal efficiency correspondingly. Generally, NaOH catalyst disrupts the plant cell walls and releases the mineral components that are physiologically bound to the plant tissue [50]. Some reductions in the K and Ca contents were also recorded which are believed to be the organic form [50]. Content of Na in the pretreated samples increased with NaOH concentration. This trend was due to the conversion of Na form NaOH to irrecoverable salts which was incorporated into the biomass by the pretreatment reactions [48, 55].

Table 1: Mineral composition of raw NGS and pretreated samples using NaOH, H_2SO_4 and deionized water

3.3 Morphological properties

Effect of pretreatment on the morphological characteristics of NGS was evaluated with SEM as shown in Figure 5. Comparing with the RNGS, changes in the particle shape was observed in the pretreated sample. RNGS has definite structure with some small particles attached to it. After pretreatment with water, the structure became clearer with large particles appearing on the surface which was due to removal of small particles during the pretreatment. Structural disruptions were observed in the ACTNGS and ALTNGS samples. The structures became eroded, loose and porous with far less particles attached to the surface. These morphological changes were due to removal of hemicellulose and possibly some parts of the cellulose by the H_2SO_4 and solubilization of lignin and portion of hemicellulose by the NaOH during the pretreatment [28, 49, 51, 5-56].

Figure 5. SEM images of raw and pretreated samples. Scanning conditions: HV (20kV), Mag (1200x). (RNGS) raw NGS, (WTNGS) water treated-Ro: 0.9, (ACTNGS) acid treated-1.5 w/w% H2SO4 and (ALTNGS) alkaline treated 1.5 w/w% NaOH

3.4 Organic composition

Biomass is generally made up of various organic compounds which consist predominantly carbon (C), hydrogen (H) and oxygen (O). The proportion of these elements varies depending on the nature and type of biomass. From the ultimate analysis of the raw and the pretreated samples (Table 2), slight changes in the elemental composition were observed. All the pretreated have higher C and lower H contents compared to the raw sample. The O contents of WTNGS and ACTNGS samples were lower than that of the RNGS while the ALTNGS samples showed increase in the O content. These changes indicate that some organic components of the biomass were washed away during the pretreatment process [49, 51]. The increase in O content of ALTNGS suggests that the samples contain more $C-O$ bonds. Van Krevelen graph (a plot of H/C versus O/C atomic ratio) was established as shown in Figure 6 to provide further insight on chemical transformations that occur during the pretreatment process. Pretreatment with H_2O and

H_2SO_4 resulted in lower H/C and O/C ratio in the samples compared to the raw sample and the points appeared toward left lower diagonal of the graph, the direction of increased energy content [28, 57]. Reduction in H/C ratio was also observed in ALTNGS samples but O/C increased which shifted the points towards the lower right hand corner of the graph, indicating a lower energy region. This further confirms the presence of more $C-O$ bonds in the samples since $C-O$ bonds have lower energy compared to $C-C$ bonds [48, 58]. This is also in agreement with the earlier trend of the energy yield observed. Therefore, the increase in O content and O/C ratio can be attributed to lignin removal in the sample during the pretreatment [60].

Table 2: Ultimate analysis of raw biomass and pretreated samples.

Figure 6. Van Krevelen plot raw and pretreated samples

3.5 Functional group analysis of raw and pretreated samples

Functional group distribution in the Napier grass before and after the aqueous pretreatment was evaluated with FTIR. Peaks were identified at different frequency as shown in Figure 7. The spectra showed two distinct regions with frequencies between 3750-2916 cm^{-1} and 1753- 615 cm^{-1}. The band between 3750 and 3421 cm^{-1} are attributed to different hydroxyl group (alcohol/phenol) stretching vibrations [60–63]. The band at 3750cm^{-1} in the RNGS became wider in WTNGS sample due to the stretching of the H-bonded hydroxyl functional group [64]. The broad peak at 3405cm^{-1} in the RNGS shifted to a higher wave number, 3656cm^{-1} and became enhanced in the ACTNGS and ALTNGS samples due to attenuation of hydrogen bonds between cellulose molecules by the acid and alkaline solvents [65]. The band at 2937 cm^{-1} is as a result of aliphatic saturated $\mathrm{C-H}$ stretching vibrations (asymmetric and symmetric methyl and methylene stretching groups) from extractives [66] which almost disappeared in all the pretreated samples, confirming the removal of extractives. In the fingerprint region (1753- 615 $\mathrm{cm^{-1}}$), the band around 1600 $\mathrm{cm^{-1}}$ in the RNGS due to the ring-conjugated $\mathrm{C=C}$ bonds of lignin [60, 61, 63, 67-69] shifted to around 1750 $\mathrm{cm^{-1}}$ in the pretreated samples. The band became improved in the WTNGS and ACTNGS while it almost leveled completely in the ALTNGS which confirms the removal of lignin in the alkaline process. New peak appeared in the WTNGS and ACTNGS samples around 1450 $\mathrm{cm^{-1}}$ which is ascribed CH_3 bending vibration in the lignin [64]. The band observed at 1200 $\mathrm{cm^{-1}}$ is an indication of $\mathrm{O-H}$ bending in the cellulose and hemicellulose [60, 61, 63, 67-69] which remained in the WTNGS but diminished in ACTNGS and ALTNGS samples suggesting removal of more hemicellulose. The frequency at 1050 $\mathrm{cm^{-1}}$ is ascribed to $\mathrm{C-O}$, and $\mathrm{C=C}$, and $\mathrm{C-C-O}$ stretching in cellulose, hemicelluloses and lignin [61, 63, 68, 69] which diminished in the following order WTNGS>ACTNGS>ALTNGS. This trend is attributed to removal of some hemicellulose and lignin in the WTNGs and ACTNGS, and ALTNGS respectively. Frequency between 800 and 600 $\mathrm{cm^{-1}}$ is attributed to aromatic $\mathrm{C-H}$ bending vibrations from the lignin [67, 68, 70] in the samples which disappeared completely in the ALTNGS.

Figure 7. Averaged FTIR spectra (auto-smoothed and auto-baseline corrected) of Napier grass samples (RNGS, WTNG-0.9, ALTNGS-1.5% and ACTNGS-1.5%)

3.6 Thermogravimetric analysis

Thermal decomposition characteristics of pretreated samples were compared with the raw sample as presented on DTG curves in Figure 8. Extractive peak (*e*) of RNGS around 478K disappeared in the all pretreated samples. Hemicellulose peak (*h*) of RNGS at 543K shifted to around 571K in WTNGS sample. The peak tends toward cellulose decomposition region which is an indication improved thermal stability due to partial solubilization of hemicellulose during the pretreatment. Hemicellulose decomposition peak was not detected in ACTNGS and ALTNGS samples. The disappearance of the peak in ACTNGS confirms substantial removal of hemicellulose during the acid pretreatments. For ALTNGS sample, it can be attributed to the alteration of the hemicellulose structure and removal acetyl groups by the alkaline solvent [71]. Cellulose degradation peak (*c*) around 600K in the RNGS shifted to 623 and 611K in WTNGS and ACTNGS samples respectively, indicating improved thermal stability. Higher cellulose reaction intensity of 10.52 wt%/K in WTNGS and 12.29wt%/K in ACTNGS was recorded compared to 7.0wt%/K of cellulose in the RNGS. This can be related to reduction in the ash content and its minerals during the pretreatment particularly the alkaline and alkaline earth metals which tend to reduce the cellulose decomposition rate during pyrolysis [21, 68]. High cellulose decomposition rate (9.79 wt%/K) was also recorded in the ALTNGS sample but at a lower temperature (595K) compared to the RNGS (600K). This observation can be attributed to level of lignin removal recorded during the pretreatment since it generally has high thermal stability. Characteristics of all the samples were similar in lignin decomposition region (*l*). No noticeable peak was observed due to low thermal decomposition characteristic of lignin which spans over a wide temperature range (above 640K). The decomposition temperature values of both raw and the pretreated samples are in good agreement with literature values [21, 71, 72].

Figure 8. DTG of RNGS, ACTNGS and ALTNGS on dry basis. (*e*) Extractives; (*h*) Hemicellulose; (*c*) Cellulose; and (*l*) lignin decompositions. Condition: nitrogen atmosphere (20 mL/min), heating rate (10 K/min).

3.7 Preliminary analysis of pretreatment effluent (leachate)

In aqueous pretreatment of biomass, secondary aqueous effluents are generated which consists mostly fine particles and parts of biomass that was solubilized during the pretreatment such as extractives, sugars, hemicellulose, lignin etc. This pretreatment coproduct is seldom utilized and generally discharged as industrial effluent [73]. Generally, a good pretreatment system is expected to require low energy, low capital and operational costs and should be conducted in such a way that coproducts have valuable downstream applications. Therefore further processing of pretreatment effluent and utilization to generate value added products become very important. Characteristic of leachate from the pure water, alkaline and acid pretreatment Napier grass is summarized in table 3.

Table 3: Characteristics of leachate from aqueous pretreatment of Napier grass

Leachate from the neutral solvent has pH value between 3.9 and 4.02 and sugar concentration from 31.47 to 34.35 g/L. The stream can be channel to biochemical conversion process to convert the sugar to bioethanol. Fine suspended solids were also observed in the leachate. This can be used as ethanol substrate in addition to the leachate to increase the ethanol concentration in the final product. Acid tolerant microbes having been developed which shows high ethanol yield under low pH condition between 2.8 and 4.7 [74-76]. Ethanol produced from this process can be used as fuel and for bio-oil stabilization during bio-oil storage and upgrading strategy. Leachate from acid pretreatment consist high concentration of sugar between 157.79 and 162.74 g/L. This present high potential for bioethanol production. However, the extreme acid condition of the effluent remains a serious challenge to microbes in biochemical process. Furthermore, neutralization of effluent under extreme acid condition has been linked to formation of high salinity leachate which deters tricarboxylic acid cycle glycolysis pathways of fermenting microorganism [35, 36]. In alkaline process, black liquor known as lignin with some sugar content was obtained. The presence of sugar is believed to have originated from extractives and partial solubilization of hemicellulose. In bio-refining integration, alkaline pretreatment may be useful where lignin separated from biomass can be upgraded directly to fuel and chemicals via catalytic process [77-80] and the residue rich in cellulose converted to ethanol through biochemical process.

3.8 Bio-oil yield and characterization

Pyrolysis products distribution obtained from the pretreated samples pyrolyzed at 600^{o}C reaction temperature, 30 °C /min heating rate and 30 mL/min nitrogen flow rate were compared with the product yield from the raw sample under the same condition as shown in Figure 9. Higher bio-oil yield was recorded from ACTNGS (38.71wt %) and WTNGS (33.28wt %) while ALTNGS produced lower yield (29.27wt %) compared to the yield from RNGS (32.06wt %). The corresponding bio-char yield from the pretreated samples was 24.21wt %, 28.05wt % and 32.15wt %. The increase in bio-oil and reduction in bio-char yields from ACTNGS and WTNGS samples can be linked to the removal of ash and its composition particularly the alkaline and alkaline earth metals during the pretreatment. This is also true for the opposite trend recorded from ALTNGS sample since Na from NaOH was believed to have converted to irrecoverable salts and became incorporated in the biomass by the pretreatment reactions [48, 55]. This tends to favor char formation during pyrolysis. Comparing the bio-oil yield with the literature, studies by Lee et al (2010) [81] on pyrolysis of Napier grass in an induction-heating reactor at different heating showed similar bio-oil yield with maximum oil yield of around 36wt% at 500^{o}C and

150°C/min heating rate. The authors concluded that higher heating rate had less impact on the pyrolysis liquid yield.

Figure 9. Pyrolysis products distribution from the raw and pretreated Napier grass samples. Biomass condition: bone dry, 0.2 to 2 mm particle size; heating rate: 30 °C/min, nitrogen flow rate: 30 mL/min; pyrolysis temperature: 600°C

Non-condensable gas yield was between 37.08 and 38.58wt%. This indicates that pretreatment has less impact on the gas yield. High non-condensable gas yield during pyrolysis is generally attributed to secondary cracking of pyrolysis vapor and further decomposition of bio-char at higher pyrolysis temperature. Physicochemical property of bio-oil from each sample is summarized in Table 4. The bio-oil collected from the all samples was dark black homogeneous liquid. The pH of the bio-oil from RNGS, WTNGS, ACTNGS and ALNGS sample was 2.95, 2.92, 2.68 and 3.26 respectively. The lower pH value of bio-oil obtained from ACTNGS sample can be attributed to the removal of base metals and alkaline compounds contained in the original biomass during the acid pretreatment [55]. Since the inorganic components of the biomass which are responsible for side reactions that normally lead to formation of organic acids [82-84] were substantially removed. The pH of bio-oil from ALTNGS sample was 3.26 which is relatively high than that of all the bio-oil from other samples. This can be connected to the removal of acetyl group and uronic acid substitution on hemicellulose during the alkaline pretreatment [55, 71]. Water content of the oil produced from RNGS, WTNGS, ACTNGS and ALTNGS was 26.02, 20.52, 17.36 and 27.47wt% respectively. About 21.14 and 33.28wt% reduction in the moisture content of bio-oil from WTNGS and ACTNGS samples respectively was recorded. On the other hand, 5.57wt% moisture increase in the bio-oil from ALTNGS sample was noted. This observation can be related to the level of demineralization recorded in the pretreatment step prior to the pyrolysis. Generally, ash content above 1.0wt% in the biomass tends to catalyze pyrolysis reaction toward formation of reaction water during pyrolysis [85, 86]. ALTNGS used in the pyrolysis had 1.13wt% ash content with increased Na composition incorporated by the NaOH compared to the RNGS (Table 1). This can therefore be responsible for the increased water content of the bio-oil. Density, viscosity and higher heating value of the oil increased with decreasing water content. Similar observations in the properties of bio-oil with respect to water content have been reported in literatures [82, 83, 86, 87]. Ultimate analysis of bio-oil reveals its carbon, hydrogen, oxygen, nitrogen and sulfur contents. The elemental compositions of the bio-oil products from both raw and pretreated samples showed similar oxygen content. Although small reduction in oxygen content was observed in the bio-oil produced from ACTNGS sample which can be attributed to the lower water content and perhaps due to the removal of hemicellulose and extractives in the pretreatment step. One would have expected that the solubilization of hemicellulose and extractives component of biomass will lead to drastic reduction in oxygen content of the product bio-oil but that was not the case. Therefore, formation of oxygenated compound during the pyrolysis does not only originate from hemicellulose and extractive but also from the cellulose and lignin component of the biomass [88].

Table 4: Physicochemical characteristics of bio-oil from raw and pretreated Napier grass samples.

3.9 FTIR analysis of bio-oil

FTIR spectra of chemical compounds in the bio-oil from raw and pretreated biomass samples are shown in Figure 10. The broad peak around 3423cm^{-1} in all bio-oil sample is an indication that samples contain chemical compound with hydroxyl group ($O - H$) such as water, alcohols and phenol [88, 89]. The peak became wider in the oil produced from the ALTNGS which can be ascribed to the high level of moisture in the oil sample. The peak at frequency around 2091cm^{-1} is due $C - H$ stretching vibration of methyl and methylene groups [88, 89] which is common to all the bio-oil samples. Stretching vibration observed at 1707 cm^{-1} in the samples is ascribed to $C=O$ which signifies the presence of aldehydes, ketones or carboxylic acids. A new peak at around 1656 cm^{-1} common to the oil from the pretreated samples particularly the samples from WTNGS and ACTNGS is a characteristic of $-C=C-$ functional group which shows that the oil samples have alkene compounds [89]. Vibration at 1384 cm^{-1}, and 1262 and 1096 cm^{-1} in the oil from RNGS became enhanced in all the pretreated samples. The former is ascribed to $C-H$ confirming the presence of compound with $C-H$ bound while the later are due to $C-O$ stretching vibration indicating alcohol and esters. The peaks at 757 and 620 are ascribed to aromatic $C-H$ bending vibrations [54, 58, 88, 89].

Figure 10. Averaged FTIR spectra (auto-smoothed and auto-baseline corrected) of bio-oil from raw and pretreated samples

3.10 GC-MS analysis of bio-oil

Further confirmation of chemical species present in the bio-oil samples was carried out with GC-MS. The chromatogram of the analysis is presented in the Figure 11. The chromatograms showed similar main characteristic peaks with various intensities at retention time around 2.28, 6.0, 11.20 and 18.0min which confirm that the bio-oils contain some similar chemical compounds. At retention time of around 26mins, another main characteristic peak was observed in the chromatogram for bio-oil sample from WTNGS and ACTNGS. This suggests the presence of new and similar chemical specie in the oils which can be linked to the changes in the original biomass composition as result of solvents during pretreatment process. The chromatograms also showed other characteristic peaks which indicate presence of additional chemical compounds in the oil. Library search using MS NIST library 2011 confirms the compounds and are summarized in Table 5. The values quoted below represent the GC-MS peak area (%). The chemical compounds identified by the common main characteristic peaks above were benzene, furfural, phenol and catechol respectively. While the peak common to bio-oil from WTNGS and ACTNGS was Levoglucosan. Other chemical species such as organic acids, aldehydes, ketones, esters and some nitrogen and sulfur containing organic compounds were also detected.

Figure 11. GC-MS chromatogram of bio-oil samples from raw and pretreated Napier grass

Table 5: Chemical compounds detected in bio-oil from raw and pretreated samples

In order to elucidate the effect of the pretreatment on the distribution of chemical compounds in the oil, the compounds were further classified as hydrocarbons (HC); value added chemical (VAC); acids, aldehydes and ketones (AAK); esters and other organic compounds (EOC); nitrogenous and sulfur containing compounds (NS) as illustrated in Figure 12 . Highest HC content was recorded in the bio-oil from ALTNGS follow by the oil from RNGS, WTNGS and the least was obtained in the oil from WTNGS and the corresponding percentage peak area was 9.0, 5.0, 2.0 and 1.5%. Generally, HC are formed during pyrolysis either from the product of partial pyrolysis or volatile compounds of the source biomass [90]. The high percentage recorded HC recorded in the oil from ALTNGS could be attributed to selective removal of lignin during the pretreatment which makes other volatile components of the Napier grass readily available for conversion during the pyrolysis. While the lower composition of HC in the oil from WTNGS and ACTNG was due to removal of some hydrocarbon component by the water and acid solvent at the pretreatment stage. The VAC chemicals which constitute phenolics (phenols and alcohols), furans, furfural and levoglucosan in the bio-oil increased with pretreatment in the following order ACTNGS>WTNGS>ALNGS>RNGS. Phenolics in the bio-oil are generally product of lignin degradation during the pyrolysis [55, 87, 90]. The high yield of phenolics in the oil from the pretreated samples could be attributed to the reduction in the ash content of the original biomass during pretreatments since the ash tends to catalyze pyrolysis reactions which generally lead to degradation and polymerization of the intermediate products [90]. Lower value of the phenolic content in the oil from ALTNGS compared to ACTNGS and WTNGS is linked to the lignin removal by the alkaline solvent during the pretreatment [8, 55, 90]. Furan, furfural and levoglucosan are degradation product of cellulose and hemicellulose [55, 87, 90]. Lower level of furfural in the oil from ALTNGS and ACTNGS compared to the oil from WTNGS sample was due to the removal of hemicellulose recorded during the pretreatment which was also evident in the thermogravimetric result and sugar concentration in the leachate. In the case of oil from RNGS, it can be attributed to the high ash level in the raw sample which generally favors side reactions that lead to formation of organic acids [55, 90]. Levoglucosan was present only in the bio-oil from WTNGS and ACTNGS feedstocks. This can also be related to the ash content in the biomass. In addition, it can also be said that the pretreatments permits the formation of a cellulose structure which lead to the production and faster withdrawal levoglucosan in the pyrolysis vapor product stream [20, 87, 90]. Decline in the AAK constituents of the bio-oil from the pretreated samples was observed which could be attributed to the combine effect of the ash and hemicellulose removals during the pretreatment since elimination of hemicelluloses from biomass does not significantly reduce content the AAK content in the bio-oil [20, 87]. The proportion of ester and other organic compounds such as pentamethoxyflvone, propanenitrile detected was 26.99, 25.34, 11.12 and 0.23% in the bio-oil from RNGS, ALTNGS, ACTNGS and

WTNGS respectively. NS detected in the bio-oil can be attributed to nitrogen and sulfur content in the parent biomass [89].

Figure 12. Classification of organic in the bio-oil from raw and pretreated NGS samples

4. Conclusions

This study provides background of different biomass pretreatment as it affect pyrolysis and pyrolysis product. It gives experimental results of different aqueous pretreatments of Napier grass and their impacts on bio-oil yield and chemical composition. The findings are summarized below:

- Deionized water and sulfuric acid significantly reduced the ash content in the Napier grass with about 64 and 80% ash reduction respectively. Deionized water was effective in leaching Na and K while sulfuric acid substantially reduced Na, K, Ca, Al and Fe. For sodium hydroxide, 40% ash removal was recorded initially but decreased as the concentration increased. This solvent was effective for the removal Si and Al. Some reduction in K and Ca were also noted but more Na element was incorporated in the sample

- All the solvents obviously removed the extractives component of the Napier grass. Partial solubilization of hemicellulose was also observed with deionized water while substantial removal of hemicellulose was detected with sulfuric acid. Sodium hydroxide was highly effective for lignin removal. Though, it appeared that some hemicelluloses were also solubilized

- Sulfuric acid produced high acidic leachate which will require neutralization. The neutralization of highly acidic leachate can be very challenging in large scale system. Sodium hydroxide generated high lignin reach leachate that can be further upgraded to fuel and chemicals which could be a very good option for biorefinery integration. Effluent from the neutral solvent has relatively high pH. The stream can be channeled back to the pretreatment process or biochemical conversion process to convert the sugar to bioethanol.

- Pretreatment using sulfuric acid and deionized water increased bio-oil yield while sodium hydroxide promoted bio-char formation. Reduction in the water content of bio-oil from samples pretreated with deionized water and sulfuric acid was also observed. All the pretreatment methods did not show a significant reduction in oxygen content of the resulting bio-oil. However, some decrease in organic acid, aldehydes and ketones content of the bio-oil from all the pretreated samples were observed. Acid and water pretreated samples produced bio-oil with high value added chemicals.

Pretreatment with the neutral solvent can be considered appropriate for the pyrolysis process as good quality bio-oil can be produced in addition to its environmental friendliness, high generation of value added chemicals and possible practical application of its effluent. Acknowledgments

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