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EFFECT OF AQUEOUS PRETREATMENT ON PYROLYSIS CHARACTERISTICS OF NAPIER GRASS

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Abstract

Effect of non-catalytic aqueous pretreatment on pyrolysis characteristics of Napier grass was investigated using thermogravimetric analyser. Increasing pretreatment severity (0.0-2.0) improved pyrolysis process. The residual mass at the end of pyrolysis for the pretreated sample was about 50% less compared to the untreated sample. Kinetics of the process was evaluated using order based model and both pretreated and untreated samples followed first order reaction. The activation energy of the pretreated samples was similar and higher than that of the raw sample which was attributed to faster rate of decomposition due removal of hetromaterials (ash, extractives and some hemicellulose) in the pretreatment stage. Finally, this pretreatment method has demonstrated effectiveness for the removal of pyrolysis retardants and will improve the quantity and quality of bio-oil yield.

Keywords: Aqueous pretreatment; severity factor; Napier grass; Pyrolysis; kinetics; TGA

1. Introduction

Efficient utilization of biomass as a source of energy continues to gain more recognition in recent times due to its renewability and potentials of replacing or reducing fossil fuel application in energy sector. The use of non-food biomass such as lignocellulosic for production of biofuels seems promising as they such as

Nomenclatures

A	Frequency factor, min^{-1}
B	Biomass
E	Activation energy, kJ/mol
g	gas phase
m_o	Initial mass of the sample, mg
m_t	Mass of the sample at any time during pyrolysis, mg
m_∞	Mass of the sample at the end of pyrolysis, mg
n	Reaction order
R	General gas constant, J/mol. K
R_o	Severity factor $t \times \exp\{(T - 100)/14.75\}$
R_s	Residual solid
s	solid phase
T	Temperature, $^{\circ}\text{C}$, K
t	Time, min
UT	Untreated
x_b	biomass conversion $(1 - \alpha_t)/(1 - \alpha_\infty)$

Greek Symbols

α_t	Mass ratio at any time, t
α_∞	Mass ratio at end of pyrolysis
β	heating rate, K/min

Abbreviations

BS	British Standard
C	Crops For the Future Research Centre
CFFRC	Carbon (%)
DTG	Derivative of Thermogravimetric
EN	European Standard
H	Hydrogen (%)
HHV	Higher heating value (MJ/kg)
N	Nitrogen (%)
NGS	Napier Grass Stem
O	Oxygen (%)
rpm	Revolution per minute (min^{-1})
S	Sulfur (%)
STA	Simultaneous thermal analyser
TGA	Thermogravimetric analyser

lignocellulosic for production of biofuels seems promising as they eliminate the fear of food insecurity and are evenly distributed across the globe. In addition, they require simple processing methods and low capital investment [1-3]. Generally, lignocellulosic biomass consist large portion of cellulose, hemicellulose and lignin. This composition varies depending on the plant species. For example, herbaceous materials such as Napier grass have around 27% lignin content, 42% cellulose and 25% hemicellulose [4-8]. However, considerable portion of the biomass is made up of extractives and inorganic component known as ash, which affect pyrolysis oil (bio-oil) in both yield and quality in addition to

some operational problems such as fouling, erosion and slagging during pyrolysis [9, 10] and therefore, pretreatment becomes an important step prior to pyrolysis.

Several biomass pretreatments such as hydrothermal pretreatment, steam explosion, chemical pretreatment and liquid hot water pretreatment, organic solvent pretreatment and biological pretreatment have been carried out mostly to aid biological conversion of biomass [11-17]. Recently, steam explosion, chemical pretreatment, torrefaction and hot water pretreatment have been applied for pyrolysis process [18-20]. Each of these methods has advantages and disadvantages. For example, steam explosion is typically carried out with saturated steam at temperature between 180-240°C [21]. It removes hemicellulose and may improve the quality of bio-oil. However, this method is characterized with high tendency of formation of toxic and degradation products in addition to the energy requirements [22]. In the chemical pretreatment, catalytic aqueous solvent such as acid, alkaline or combination acid and alkaline solvents are used. Acid solvent selectively removes hemicellulose which leads to improvement in bio-oil physicochemical properties [20, 22]. Some level of lignin extraction also occurs in this process which may have negative effect on the bio-oil yield since lignin is an important component of the pyrolysis feedstock. Similarly, alkaline solvent is very effective on the delignification and thus show little positive impact on bio-oil yield and quality [20, 22]. In addition, High cost of the catalyst, corrosion resistant equipment and requirement for effluent neutralization remain a challenge [22, 23]. Torrefaction has been identified to promote formation of bio-char leading to reduction in bio-oil yield [18, 19]. The use of liquid hot water which is non-catalytic is capable of selective removal of hemicellulose, alkaline and alkaline metals [20, 22]. However, issues of energy and water input need to be addressed [22]. Generally, a good pretreatment method should be eco-friendly and should have low energy demand and low capital and operating costs. Therefore, the non-catalytic aqueous solvent at room temperature seem promising, hence the need for investigation.

The objective of this study was to evaluate the effect of non-catalytic aqueous pretreatment on pyrolysis of Napier grass using Thermogravimetric approach.

2. Experiment

Fresh Napier grass stem chopped 6 to 8cm was collected from Crops for the Future Research Centre (CFFRC) field and transported in plastic bags to N-Block research building of University of Nottingham Malaysia campus. The materials were oven dried at 105°C for moisture content determination using BS EN 14774-1 [24] standard. 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. Volatile matter and ash content on dry basis were determined according BS EN 15148 [25] and BS EN 14775 [26] 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 [27]. Determination of elemental composition was carried out using CHNS analyser, LECO Corporation USA. Non catalytic aqueous pretreatment was studied with deionized water at severity factor between 0-2 according to Eq. (1), liquid-solid mass ratio of 1:5 and agitation speed of 100rpm. Pyrolysis study was

carried out in thermogravimetric analyser (TGA) PerkinElmer Simultaneous thermal analyser (STA) 6000 in nitrogen atmosphere flow rate 20 mL/min at temperature between 300-1100K and heating rate of 10 K/min. About 10.0 mg (particle size of less than 0.2 mm) of sample was used in the pyrolysis study [28].

$$R_o = t \times \exp\left[\frac{T-100}{14.75}\right] \quad (1)$$

where, t is the pretreatment time in minutes, T is the pretreatment temperature in °C.

3. Results and Discussion

Raw Napier grass stem (NGS) has around 75% moisture at harvest. The result of proximate and ultimate (CHNSO) analyses on dry basis is shown in Table 1. The volatile matter and ash content were found to be 81.51 and 1.75 wt% respectively. The elemental composition Carbon, hydrogen, nitrogen, sulfur and oxygen (wt% dry basis) were 51.61, 6.01, 0.99, 0.32 and 41.07 correspondingly. Generally, carbon content of biomass is directly linked to its cellulose, hemicellulose and lignin. With respect to lignin, NGS is expected to have some good level of lignin content due to its high carbon content.

Table 1. Proximate and ultimate analyses of raw Napier grass stem (NGS).

Property	Value
<i>Proximate analysis (wt %)</i>	
Moisture content ^a	75.27
Volatile matter ^b	81.51
Ash content ^b	1.75
Fixed carbon ^c	16.74
Higher heating value (MJ/kg)	18.11
<i>Ultimate analysis (wt %)</i>	
Carbon ^b	51.61
Hydrogen ^b	6.01
Nitrogen ^b	0.99
Sulfur ^b	0.32
Oxygen ^c	41.07

^aAt harvest, ^bDry basis, ^cBy difference. Each value is an average of three replicate, the standard deviations are within 3%

Thermogravimetric analysis showed thermal decomposition of various components of raw Napier grass with different peaks as presented in Fig. 1. Point (a) 333K indicated evaporation of water from the sample. Peak (b) at 478K may be attributed to decomposition of extractives. While (c) and (d) correspond to decomposition of hemicellulose at temperatures 543K and cellulose at 600K respectively. Beyond 600K, Point (e), signifies decomposition of lignin. This is in good agreement with literature value of 373-523K, 523-623K, 623-773K and above 773K for decomposition of extractives, hemicellulose, cellulose and lignin correspondingly [29]. No noticeable peak was observed in the lignin

decomposition region. Consequently, it can be deduced that lignin content of NGS has uniform decomposition over the temperature.

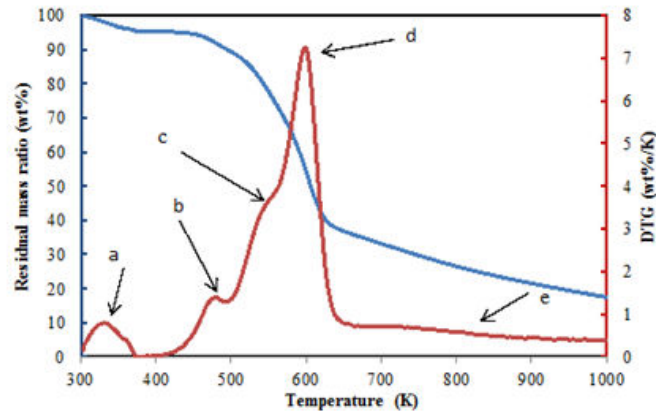


Fig. 1. Residual mass ratio and DTG of raw Napier grass.
(a) Water evaporation; (b), (c), (d) and (e) extractives, hemicellulose, cellulose and lignin decompositions respectively.

Figure 2 shows residual weight from TGA analysis. Residual mass decreased with increasing pretreatment severity which translates to more volatile yield. About 50% reduction in residual weight was recorded with pretreated samples compared to the raw sample. This means substantial amount of extractives and inorganic components (ash) were successfully removed in the pretreatment process.

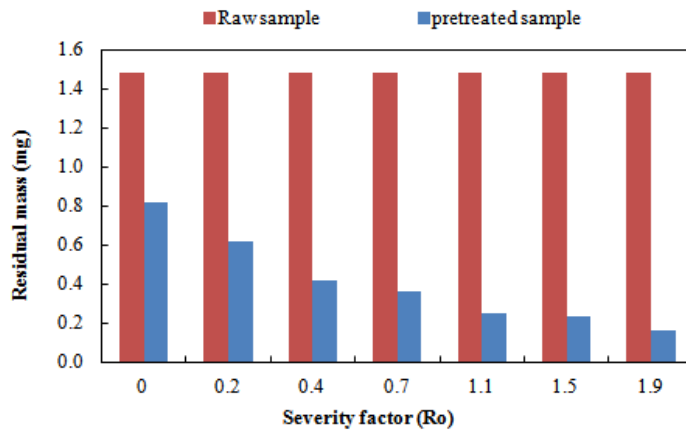


Fig. 2. TGA residual mass against pretreatment severity factor.
Initial sample mass (10 mg), nitrogen atmosphere (20 mL/min) and heating rate (10 K/min). Each data is an average of three replicate and standard deviation is within 3%.

In DTG distribution curves (Fig. 3), a peak appeared around 571K for the all pretreated samples. This may be associated to decomposition of hemicellulose. Comparing with the untreated sample, the peak tends toward cellulose

decomposition region and may be due to less hemicellulose remaining in the system since substantial part of it may have been solubilized during the pretreatment. Before this point, no noticeable peak was observed. This further confirms successful removal of extractives. The main peak which is the cellulose decomposition appeared around 630K and reaction intensity between 9-11w%/K while that of raw sample was at 600K and 7w%/K. This improvement in cellulose reaction intensity may be related to reduction of ash and its minerals during the pretreatment particularly the alkaline and alkaline earth metals.

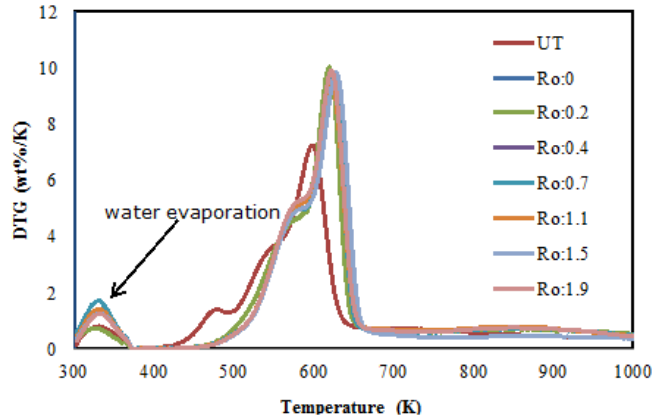


Fig. 3. DTG distribution versus pretreatment severity factor. (UT) untreated sample; nitrogen atmosphere (20 mL/min); heating rate (10 K/min).

The TGA decomposition reaction can be represented by Eq. (2) as shown below.



where *B*: solid biomass; *V*: volatiles and *Rs*: residual solid. *k*: decomposition rate constant.

From solid state chemistry, the rate of reaction can be written as [30]

$$\frac{dx_b}{dt} = k(T)f(x_b) \tag{3}$$

The rate constant *k* is function of temperature and generally represented by the Arrhenius equation and *f* (*x_b*) is expressed inform of reaction order model. Eq. (3) becomes

$$\frac{dx_b}{dt} = (1 - x_b)^n \times Ae^{-\frac{E}{RT}} \tag{4}$$

For non-isothermal process at constant heating rate (β), Eq. (4) can be transformed to

$$\frac{dx_b}{dt} = \frac{dx_b}{dT} \times \frac{dT}{dt} = (\beta) \frac{dx_b}{dT} = (1 - x_b)^n \times Ae^{-\frac{E}{RT}} \tag{5}$$

Taking natural logarithm of Eq. (5) and rearrange we have Eq. (6). A plot of right hand side versus 1/T will give a straight line for a particular reaction order.

The kinetic parameters; frequency factor, A (min^{-1}) and activation energy, E (kJ/mol.) can be obtained from the intercept and slope of the graph. R is the general gas constant 8.314J/mol. K

$$\ln \left[\frac{(\beta) \frac{dx_b}{dT}}{(1-x_b)^n} \right] = \ln A - \frac{E}{R} \times \left[\frac{1}{T} \right] \quad (6)$$

$$x_b = \text{conversion ratio} = \frac{m_o - m_t}{m_o - m_\infty} = \frac{1 - \left(\frac{m_t}{m_o} \right)}{1 - \left(\frac{m_\infty}{m_o} \right)} = \frac{1 - \alpha_t}{1 - \alpha_\infty} \quad (7)$$

where m_o , m_t , and m_∞ equal initial sample mass, mass remaining at any time (t) and residual mass at the end of pyrolysis respectively.

The experimental data for the raw Napier grass was first fitted to Eq. (6) for determination of kinetic parameters which was used as basis for comparison with the pretreated sample. Table 2(a) gives the summary of correlation coefficient (R^2 value), slope and intercept for different reaction order. From the R^2 , pyrolysis reaction follows first order kinetics. The pre-exponential factor and activation were $2.11 \times 10^4 \text{ min}^{-1}$ and 47.97 kJ/mol. respectively. The activation energy of pretreated samples was between 78.36-83.6 kJ/mol. Table 2(b), and higher than that of the untreated sample. This means that the pretreated samples have less heteromaterials which make the reaction sensitive to temperature change and proceeds at faster rate compared to the raw sample where extractives and inorganic components tend to retard the rate of reaction.

Table 2(a). Summary of kinetic parameter of raw Napier grass sample for different reaction order.

Reaction order (n)	R^2 value	Slope	Intercept
0	0.9297	-4450.5	7.0978
0.5	0.9593	-5110.6	8.5283
1	0.9971	-5769.8	9.9571
2	0.9675	-7088.3	12.8150
3	0.9512	-8406.8	15.6720

Table 2(b). Summary of kinetic parameter of raw and pretreated samples for the first order reaction. Gas constant (R) = 8.3142 J/mol.K.

Ro	Slope ($-E_A/R$)	Intercept (ln A)	A (min^{-1})	E_A (kJ/mol.)
UT	-5769.80	9.96	2.11E+04	47.97
0.0	-10005.00	21.53	2.24E+09	83.18
0.2	-9424.80	16.00	8.89E+06	78.36
0.4	-9957.00	16.89	2.17E+07	82.78
0.7	-9555.40	16.20	1.08E+07	79.45
1.1	-10028.00	17.05	2.54E+07	83.37
1.5	-10051.40	16.83	2.04E+07	83.57
1.9	-10055.18	17.10	2.67E+07	83.60

4. Conclusion

Pyrolysis of Napier grass was carried out using thermogravimetric analyser. Thermal decomposition of the material occurred in different phases. Water evaporation, decomposition of extractives, hemicellulose and cellulose was at 333, 478, 543 and 600 K respectively. Effect of non-catalytic aqueous pretreatment on pyrolysis characteristics of Napier grass was investigated. Increasing pretreatment severity improved pyrolysis process. The residual mass at the end of pyrolysis was about 50% less for the pretreated samples compared to the untreated sample. Kinetics of the process was evaluated using order based model and both pretreated and untreated samples followed first order reaction. The activation energy of the pretreated samples was similar and higher than that of the raw sample which was attributed to faster rate of decomposition due to removal of inorganic materials, extractives and some hemicellulose during the pretreatment. This pretreatment method has demonstrated ability to improving the quantity and quality of bio-oil since biomass ash and extractive normally lower pyrolysis temperature which favor char formation and reaction water. Hemicellulose depolymerized to acids, aldehydes and ketones which affect physicochemical properties of the bio-oil and subsequent upgrading process through catalyst deactivation.

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