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Torrefaction and Combustion of Ligno-Cellulosic Biomass

Joseph Kihedu*

Department of Mechanical and Industrial Engineering, University of Dar es Salaam, P. O. Box 35131, Dar es Salaam, Tanzania.

Abstract

Torrefaction of biomass and ligno-hemicellulosic compounds followed by combustion of torrefied samples was conducted by using a TGA. Cellulose exhibited highest thermal stability during torrefation at 473 K. Hemicellulose attained 48% decomposition after torrefaction at 523 K while lignin decomposition was limited to 65% after torrefaction at 573 K. Co-torrefaction ligno-hemicellulosic compounds followed a similar trend for torrefaction behavior of biomass samples. Morphology changes in torrefied cellulose and biomass were notable on fiber shrinkage basis while hemicellulose disintegrated into smaller. However, no significant morphology change was observed on lignin. HHV increased with the increase in torrefaction temperature however torrefaction at 573 K resulted into decrease in HHV for biomass and co-torrefied ligno-hemicellulosic compounds. Optimal torrefaction temperature was observed to be 523 K where average mass loss of 34% resulted in energy yield of 75%. Torrefied samples exhibited slightly slower combustion than pyrolyzed samples. Combustion reactivity of torrefied biomass, hemicellulose, cellulose and lignin were realized to be 15%/min, 21%/min, 18%/min and 14%/min, respectively.

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Torrefaction, Combustion, Biomass, Hemicellulose, Cellulose, Lignin

1. Introduction

Torrefaction process refers to biomass densification process through mild thermal treatment under very low or no oxygen environment [1]. Typical temperature range used for the process is between 473 K and 573 K. Torrefaction differs from pyrolysis process in which higher temperatures used may results into total removal of volatile matters. The process reduces moisture content, improves heating value, improves grind-ability, and harmonizes feedstock properties. Therefore torrefied biomass can be used for co-firing with pulverized coal and gasification in entrained flow reactors [2]. As opposed to hygroscopic raw biomass, torrified biomass is hydrophobic and therefore storable.

* Corresponding author. Tel.: +255-222-410573; fax: +255-222-410119.
E-mail address: kihedu@udsm.ac.tz.

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Compositions of lignin, cellulose and hemicelluloses are crucial factors in biomass reactivity [3,4]. Cellulose decomposes fast between 300 °C and 400 °C while lignin decomposes slowly from 250 °C to 500 °C [5]. During torrefaction, major part of hemicelluloses is decomposed; however the extent of decomposition for lignin and cellulose depends on the temperature ranges at which torrefaction is carried out [1]. Besides, analysis of combustion behaviours of torrefied biomass has gained little attention so far [2]. It is therefore important to investigate on torrefaction behavior of ligno-hemicellulosic biomass. In this study, torrefaction behaviours and morphology changes were experimentally investigated. Energy yield in torrefied samples in addition to combustion characteristics were also analyzed.

2. Experimental methods

2.1. Samples used

Biomass A (*Pterocarpus angolensis*) and biomass B (*Afrocarpus gracilior*) milled by using Shimadzu Grinder to 150 μm were used. Lignin supplied by Kanto Chemical Co. Inc, as well as microcrystalline cellulose and hemicellulose supplied by Sigma-Aldrich Chemie GmbH, were used. Proximate and ultimate analyses of these samples are shown in Table 1. Torrefaction was conducted for; biomass A, biomass B, lignin, cellulose and hemicellulose. In this paper, biomass M refers to mixture of lignin, cellulose and hemicellulose at 33%, 42%, 25% ratio, respectively [5,6].

Table 1. Proximate and ultimate analysis of the samples

Sample	Proximate analysis (wt, %)				Ultimate analysis (wt, %)			
	As received	Dry basis			Dry ash and free basis			Balance
	Moisture	Volatile matter	Fixed Carbon	Ash	C	H	N	O
Biomass A	5.81	74.64	22.29	3.07	50.52	6.45	0.10	42.89
Biomass B	7.63	71.94	23.52	4.54	47.56	5.85	0.17	46.51
Hemicellulose	5.12	90.46	9.49	0.05	44.97	6.23	0.13	48.67
Cellulose	4.96	85.14	14.86	0.01	45.34	6.97	0.08	51.39
Lignin	2.23	38.62	55.64	5.74	60.58	5.14	0.27	33.99

2.2. Torrefaction and combustion experiments

Torrefaction of about 10 mg samples was conducted by using Rigaku 8120 TGA under N_2 flow at a rate of 150 mL/min. Heating rate from ambient temperature to 380 K was set at 20 K per minute. Then, samples were held at a constant temperature of 380 K for 10 minutes to remove moisture. Heating to torrefaction temperature i.e. 473 K, 523 K or 573, was set at 20 K per minute. Then, torrefaction proceeded for 3600 s. Combustion experiments started with torrefaction process however, constant temperature torrefaction was followed by rapid heating at 50 K per minute to limit further decomposition before constant temperature combustion was conducted at 1173 K. During combustion, N_2 flow was replaced with air at 50 mL/min. For the purpose of comparison, combustion of samples pyrolyzed at 20 K per minute but without torrefaction, was also conducted at 1173. Morphology of untreated and torrefied samples was investigated by using Scanning Electron Microscope (SEM), EDAX Genesis model. For the purpose of morphology investigation, torrefaction of the samples was conducted at 573 K for 3600 s. After torrefaction, the samples were allowed to cool under N_2 purging. Before SEM investigation, samples were carbon-coated in order to improve their electrical conductivity and hence visibility during SEM investigation.

2.3. Analytical procedures

Decomposition ratio during torrefaction and combustion X (%), was derived from mass of the sample before experiment m_o (g) and instantaneous residual mass m (g) as follows;

$$X = (1 - m/m_o) \times 100 \quad (1)$$

According to Parikh et al., [7], higher heating value HHV_f (MJ/kg) can be estimated as follows;

$$HHV_f = 0.3536 \times FC + 0.1559 \times VM - 0.0078 \times AS \quad (2)$$

where FC represent fixed carbon (1.0 to 91.5%), VM is the volatile matter (0.92 to 90.6%) and AS indicates ash content (0.12 to 77.7%) . The average absolute error is 3.74% and bias error is 0.12%.

Energy yield ηe was calculated from heating values for torrefied samples HHV_t and heating value for untreated sample HHV_u by using the following equation;

$$\eta_e = (HHV_t/HHV_u \times X) \times 100 \quad (3)$$

Average combustion reactivity R between the two combustion stages, X_1 and X_2 as follows;

$$R = \frac{\int_{t_{x_1}}^{t_{x_2}} \frac{\left(\frac{dX}{dt}\right)(t)dt}{1-X(t)}}{t_{x_2} - t_{x_1}} \quad (4)$$

where t_x is the time when conversion X was attained while X_1 and X_2 were taken to be 90% and 30% in order to avoid obscuring of the global trend.

3. Results and discussion

3.1. Torrefaction characteristics

Fig. 1(a) shows decomposition characteristics during torrefaction at 473 K. Decomposition is indicated by the second decay which appears after drying process. Biomass A, Biomass B and Lignin samples slight decomposed to around 86% of the initial mass. Hemicellulose and Biomass M, decomposed to around 93% while cellulose remained almost stable. Decomposition characteristics during torrefaction at 523 K are presented in Fig. 1(b). Hemicellulose decomposed to around 50% while Biomass A and Biomass B decomposed to around 66%. Biomass M and Lignin decomposed to 72% and 77%, respectively. Cellulose slightly decomposed to 92% confirming thermal stability of cellulose at lower temperature ranges as opposed to the generalized concept that cellulose has lower thermal stability [4,5].

Fig. 1(c) shows decomposition characteristics during torrefaction at 573 K. Cellulose and Hemicellulose decomposed by 13% and 18%, respectively. Biomass B and Biomass M decomposed to around 32% while Biomass A decomposed to 41%. Lignin decomposition was limited to 65%, indicating thermal stability as reported by other researchers [4,5]. Co-torrefaction of ligno-hemicellulosic compounds and Biomass M followed almost a similar trend.

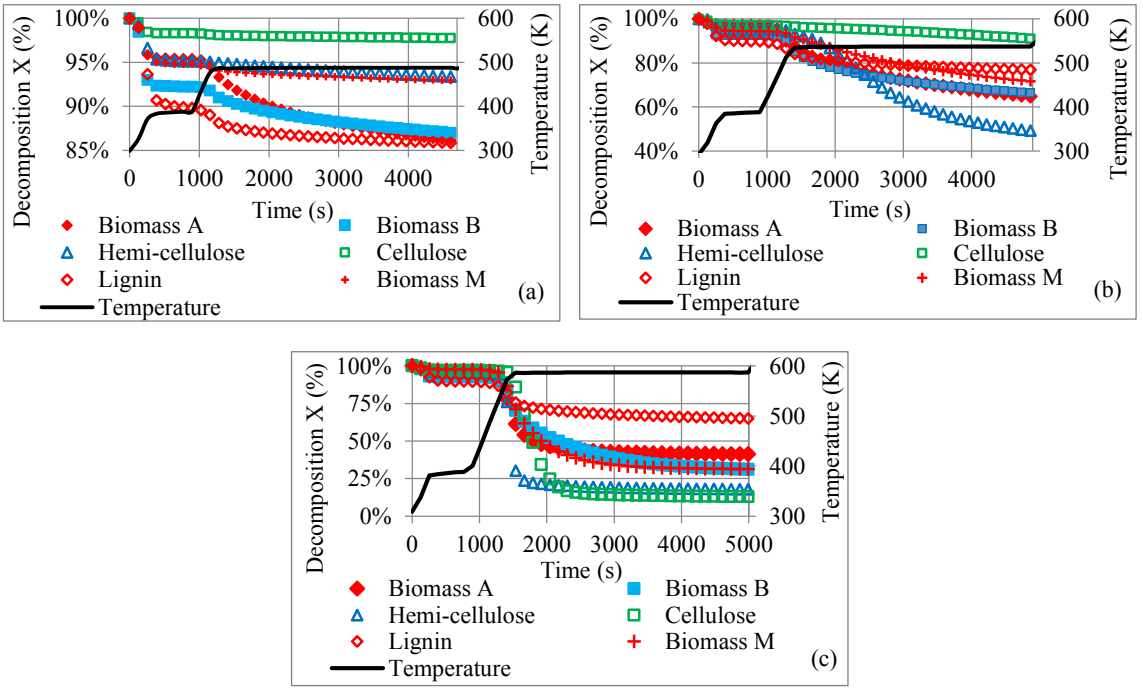


Fig. 1. Decomposition characteristics during torrefaction (a) at 473 K; (b) at 523 K; (c) at 573 K

3.2. Morphology changes and energy recovery

Fig. 2 and Fig. 3 show that after torrefaction at 573 K, morphology changes in Biomass A are notable on fiber shrinkage basis. Similar phenomenon was observed for torrefied Biomass B. Fiber size shrinkage on biomass samples is associated with decomposition of the cellulose rich primary wall [8,9]. Menwhile, hemicelluloses disintegrated into smaller particles while cellulose also exhibited significant fiber shrinkage after torrefaction. Limited change occurred for lignin confirming thermal stability below 573 K [4,5].

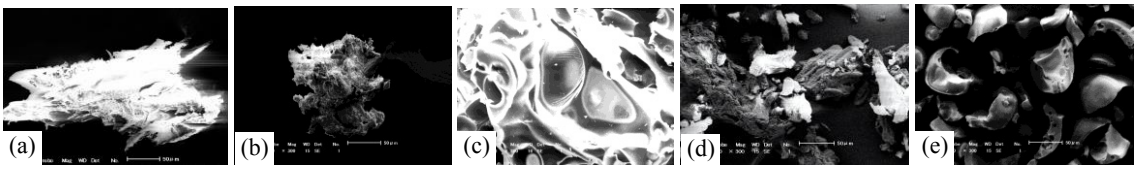


Fig. 2. SEM photo for untreated (a) Biomass A; (b) Biomass B; (c) Hemicellulose; (d) Cellulose; (d) Lignin

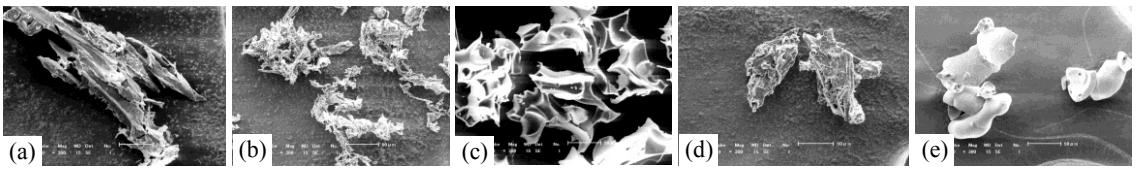


Fig. 3. SEM photo for torrefied (a) Biomass A; (b) Biomass B; (c) Hemicellulose; (d) Cellulose; (d) Lignin

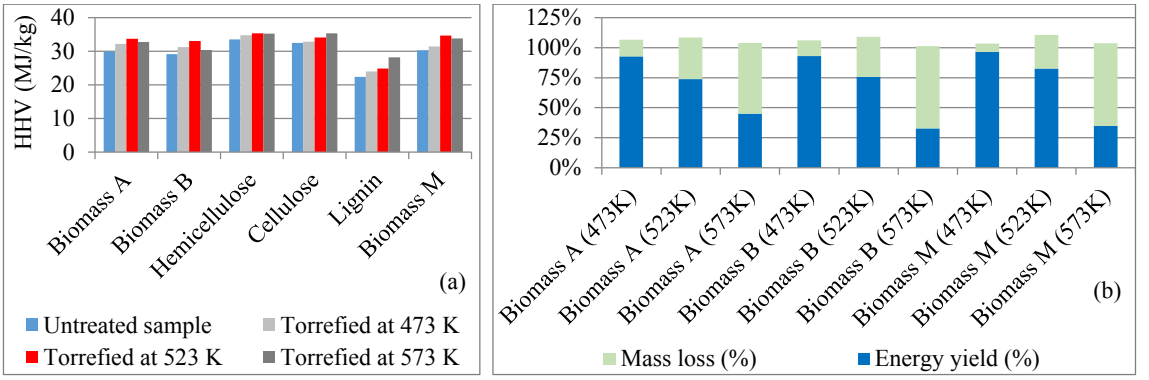


Fig. 4. (a) HHV for untreated and torrefied samples; (b) Energy yield and mass loss for torrefied samples.

Fig. 4(a) shows that HHV for torrefied samples is higher than HHV for untreated samples [1,10]. HHV increases with the increase in torrefaction temperature, especially for cellulose and lignin. However, torrefaction at 573 K resulted into reduction of the HHV for the case of Biomass A, Biomass B and Biomass M. Fig. 4(b) shows energy yield in torrefied biomass samples in parallel with mass loss. For an average mass loss of 34% and energy yield of 75%, the results suggest that 523 K can be considered as optimal torrefaction temperature for biomass on the basis of energy yield.

3.3. Combustion characteristics

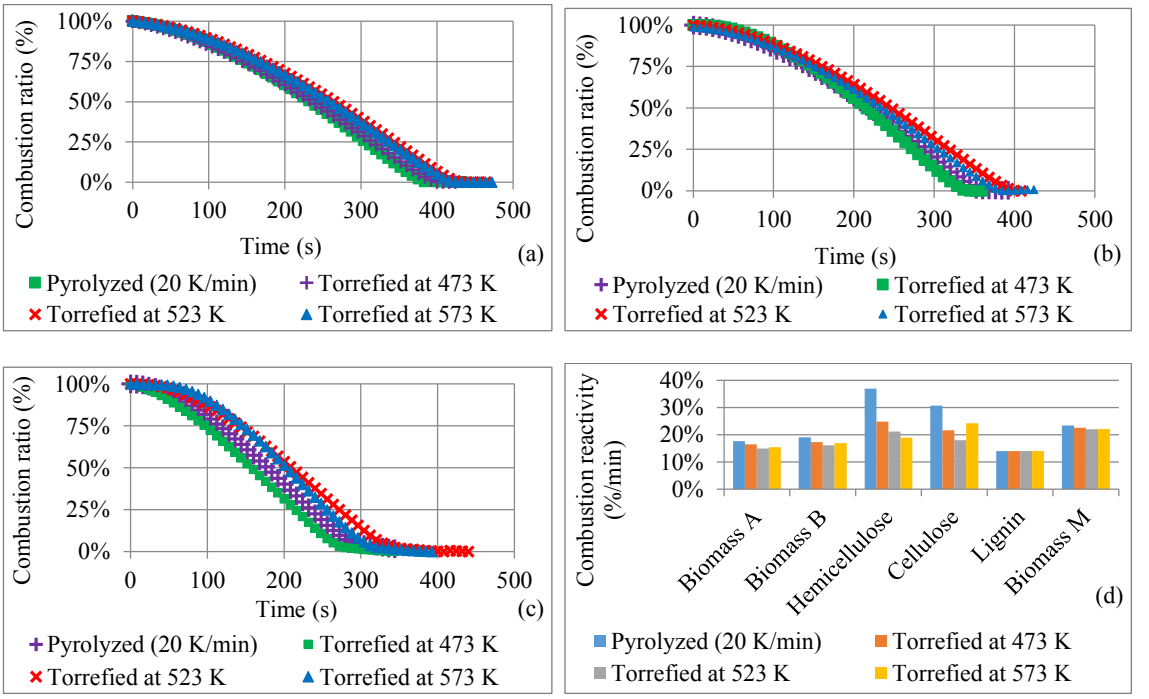


Fig. 5. Combustion characteristics (a) biomass A; (b) biomass B; (c) biomass M; (d) reactivity

Fig. 5(a) through Fig. 5(c) shows that combustion process took about 400 s for biomass A and biomass B while biomass took 300s. Torrefied samples exhibited slightly slower combustion than pyrolyzed samples. Rapid combustion of pyrolyzed samples is associated with higher porosity resulting from fast decomposition as opposed to low porosity in torrefied samples [2,11]. Reactivity decrease with increase in torrefaction temperature however slight increase was observed after torrefaction at 573 K (Fig. 5(d)). Reactivity of biomass A, biomass B, hemicellulose, cellulose and lignin torrefied at 523 K were 15%/min, 16%/min, 21%/min, 18%/min and 14%/min, correspondingly.

4. Conclusion

Cellulose exhibited thermal stability during torrefation at 473 K while lignin decomposition was limited to 65% during torrefaction at 573 K. Co-torrefaction of ligno-hemicellulosic constituents followed a similar trend for torrefaction behavior of biomass samples at 573 K. Fiber size shrinkage were observed after torrefaction of biomass and cellulose. HHV increases with the increase in torrefaction temperature however torrefaction at 573 K resulted into reduction of the HHV for biomass samples. Torrefied samples exhibited slightly slower combustion than pyrolyzed samples. Combustion reactivity of biomass, hemicellulose, cellulose and lignin torrefied at 523 K were 15%/min, 21%/min, 18%/min and 14%/min, correspondingly.

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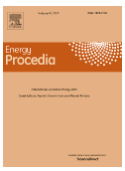
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Biography

Dr. Joseph Kihedu obtained his Ph.D. in 2013 from Nagoya Univerity in Japan. Currently, he is a Lecturer and Coordinator for MSc in Renewable Energy programme at the University of Dar-es-Salaam, Tanzania. Dr. Kihedu has published a number of papers in the area of biomass gasification, pyrolysis and torrefaction.