Chapter 32
Characterization of Pyrolysis Kinetics for the Use of Tropical Biomass as Renewable Energy Sources

P. Ndalila, G. R. John and C. F. Mhilu

Abstract Tropical biomass such as rice husks, sugar bagasse, coffee husks and sisal waste are among typical biomass wastes abundant in most of the tropical countries. However, despite their enormous potential as energy sources, they are hardly studied and their thermal characteristics are still not well known. The purpose of this work is to determine the thermochemical characteristics and pyrolysis behavior of these selected biomasses. Proximate, ultimate and heating value analyses were carried out on the samples. Results show that all biomass have a range of, volatile contents (50–80 % w/w), fixed carbon (10–20 % w/w), ash content (<3 % w/w), carbon (50–56 % dry basis) low nitrogen (0.7–1.3 % dry basis) and sulphur (<0.1 wt % dry basis) contents with heating value (HHV 14–18 MJ/kg). The biomasses were thermally degraded through thermogravimetry analysis and their characteristics such as devolatilisation profiles and kinetics parameters (activation energy *E*, and frequency factor *A*) were determined, in an inert atmosphere. It is found that the kinetic parameters obtained can predict not only global devolatilization of biomass pyrolysis but also can predict the pyrolysis pathway of cellulose in the target biomass.

Keywords Tropical biomass · Pyrolysis · Kinetics

Short Introduction

Although typical tropical biomass wastes as rice husks, sugar bagasse, coffee husks and sisal have enormous potential as energy sources, they are hardly studied and their thermal characteristics are still not well known. The purpose of this work is to

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determine the thermo-chemical characteristics and pyrolysis behavior of these selected biomasses, where the proximate, ultimate and heating value analyses were carried out on various samples. It is found that the kinetic parameters obtained can predict not only global devolatilizationof biomass pyrolysis but also can predict the pyrolysis pathway of cellulose in the target biomass.

Introduction

Tropical biomasses are among renewable energy resource available in tropical countries. These resources are from agricultural crop residues and forestry plantation or natural. The estimate form Tanzania harvest annually is 1.2 million m^3 of forests plantation (not waste) and 12.604 million tones of agricultural waste (Kamwenda and Mkeya 2000). These resources can have high potential use as alternative source of fuel since are still not in use intensively for commercial form, regarding that the present source in the world fossil fuels are nearly exhausted, where is estimated to be able to sustain reserves availability for the next 40 years for petroleum and 60 years for natural gas (Mkilaha and John 2001). The transport sector accounts high consumption, of around 97 % of liquid fuel (Economy Watch 2010). Also importation cost and environment emission of fossil fuel is a problem. From this respect, liquid fuel need to be generated from other resources, since currently it is from non renewable sources. Pyrolysis is the promising route to produce liquid fuels from biomass.

The technology of pyrolysis of biomass has been assessed as a promising route for liquid fuel production. However, uncertainties remain related to both production and utilization of technology (Chiaramont et al. 2005). Therefore, for the design of a conversion system that suits specific characteristics of the biomass, the material need be fully characterized. Pyrolysis kinetics is among the way that can lead to a dynamic and static condition of the process. During the dynamic condition, pyrolysis temperature is progressively increased with increasing heating time using a specified heating rate, while static condition maintains a selected constant temperature in a pyrolyzing reactor (Weerachanchai et al. 2010).

Kinetics of Biomass Pyrolysis

Materials

Characteristic properties of four selected tropical biomasses listed in Table 32.1 presents the proximate and ultimate analysis found of the biomass samples using ASTM as standards. The high hydrocarbons and less oxygen content are to be highlighted, together with high heating value of both tropical biomasses, compared

Table 32.1 Biomass properties analysis for rice husks, sugar bagasse, coffee husks and sisal pole (Wilson et al. 2011)

	ASTM standard	Rice husks	Sugar bagasse	Coffee husks	Sisal pole
Proximate analysis (%)					
Moisture	ASTM E-949	8.80	9.00	6.70	10.10
Volatile matter	ASTM E-872	59.20	80.50	83.20	79.30
Fixed carbon	By difference	14.60	16.20	14.30	14.60
Ash	ASTM E-1755	26.20	3.30	2.50	6.10
Ultimate analysis (%), *dry basis*					
C	ASTM E-777	45.60	48.10	49.40	47.00
H	ASTM E-777	4.50	5.90	6.10	6.00
N	ASTM E-778	0.19	0.15	0.81	1.66
O	By difference	33.40	42.40	41.20	39.10
Cl	ASTM D-6721	0.08	0.07	0.03	0.05
S	ASTM E-775	0.02	0.02	0.07	0.13
Higher heating value (MJ/kg)		13.24	17.33	18.34	17.35
"H:C" Ratio		0.13	0.12	0.12	0.13
"O:C" Ratio		0.94	0.88	0.83	0.83

to rice husks. The carbon and hydrogen contents are a good indicative of hydrocarbons content that are to be released during pyrolysis (Tsamba et al. 2006). It was also found that, content of nitrogen, sulphur, and chlorine are very small for all biomass. On the basis of elemental composition, coffee husks exhibited high energy content due to their higher H:C ratio with relatively low O:C ratio.

Pyrolysis Kinetics

Pyrolysis kinetics provides important information for the engineering design of a pyrolyzer or a gasifier. It also shed light on the different processes in a pyrolyzer that affect product yields and composition. To optimize the process parameters and maximize desired yields, this knowledge is of key important (Basu 2010).

Typical approach to the kinetics of thermal decomposition of a biomass is dividing the volatile evolution into a few fractions—lumps, each of which is represented by a single first-order reaction. These lumps are assumed to be non-interactizng and evolved by independent parallel reactions (Ledakowicz and Stolarek 2002).

If pyrolysis is performed at a constant heating rate β (K/min), the first-order rate can be expressed in the following form.

Biomass $\rightarrow$ Volatile$_i$ $i = 1, 2, 3, \ldots$n

$$\frac{dV_i}{dT} = \frac{k_i}{\beta}\left(V_i^* - V_i\right) \tag{32.1}$$

where V_i^* is the ultimate yield of the ith volatile $(\tau \rightarrow \infty)$, V_i is the accumulated amount of evolved volatiles from lump i up to time τ, k_i is the rate constant, which depends on temperature according to the Arrhenius equation.

$$k_i = A_i \exp(-E_i/(RT)) \tag{32.2}$$

where E is the activation energy (kJ/mol), R is the common gas constant, T is the temperature (K), and A is the frequency factor (s^{-1}).

At the peak temperature at which volatile evolution reaches a maximum (T_{max}), the time derivative of the reaction rate should be equal to zero. The values of T_{max} of the volatile lumps at different heating rates will be determined from peak-resolution curves (DTG). Rearrangements the two equations, final form of equation will allows to determine kinetic parameters as follows;

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \ln\left(\frac{RA_i}{E_i}\right) - \frac{E_i}{RT_{max}} \tag{32.3}$$

The parameters E_i and A_i can be determined from the slope and intercept of a linear plot of $\ln(\beta/T_{max}^2)$ vs. $1/T_{max}$ at various heating rates.

Thermogravimetric Analysis

Themogravimetric test were performed with thermogravimetric analyzer (TGA) type NETZSCH STA 409 PC Luxx. High purity nitrogen (99.95 %) was used as the carrier gas and the flow rate was 60 ml/min. About 30 mg of sample with average particle size of less than 2 mm was put in the crucible each time and heated from 35 to 1,000 °C with different heating rate ranging from 5 to 40 K/min. Calculated thermogravimetric output from the TGA software was obtained.

Results and Discussion

Biomass Decomposition Profiles

Figure 32.1, 32.2 presents the TG and derivative TG (DTG) profiles showing the thermal degradation characteristics of rice husks, sugar bagasse, coffee husks and sisal pole at a heating rate of 10 °C/min. The TG profiles show the typical degradation profile for biomasses with well demarked regions for moisture release, devolatilization and char degradation. These differences play an important role in the pyrolysis of these materials and respective product yields.

Figure 32.1, show the weight loss observed for dried samples of rice husks, coffee husks, sisal pole and sugar bagasse, at a heating rate of 10 K/min

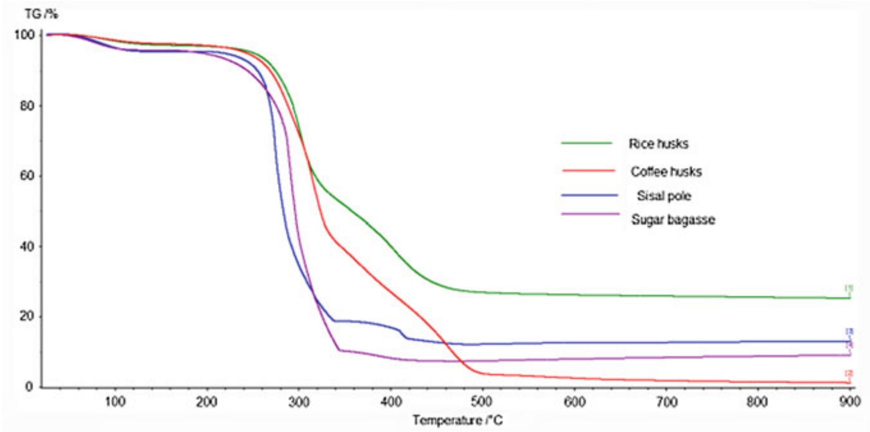

Fig. 32.1 Weight loss from the thermal decomposition of coffee husks, sugar bagasse, sisal pole and rice husks at 10 K/min

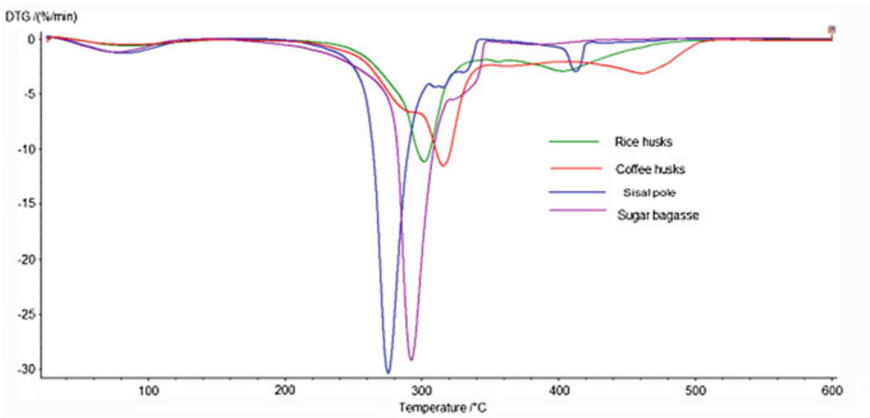

Fig. 32.2 Weight loss rate from the thermal decomposition coffee husks, sugar bagasse, sisal pole and rice husks at 10 K/min

(i,e. 5–10 K/min for pyrolysis process). The temperature interval in which each biomass sample experiences the greater mass loss is different from one to another, these intervals are 250–510, 240–440, 240–450 and 230–480 °C, where about 88.7, 83.06, 79.45 and 68.74 % of the total volatiles weight were released in coffee husks, sugar bagasse, sisal pole and rice husks, respectively. The volatiles yield is greater in coffee husks compared to both rice husks, sisal pole and sugar bagasse. Sugar bagasse have comparably much volatile matter content than sisal pole and rice husks but lower than coffee husks, the same for sisal pole than rice husks. The char yield is inversely proportional to the volatiles yield.

Figure 32.2 show the DTG profiles where, sugar bagasse have similar decomposition to sisal pole but with slightly different maximum temperature of

292 and 275 °C, and coffee husks have similar decomposition to rice husks with slightly different maximum temperature 315 and 302 °C.

Kinetic Analysis of Biomass Pyrolysis

For kinetics parameters determination, different values (as signed to the respect curve) of heating rate (β) were used (5–40 K/min) and is observed that the DTG curves for all biomasses at these various heating rates, shifts the position of the peak extreme (T_{max}) to a higher temperature region as heating rate increasing.

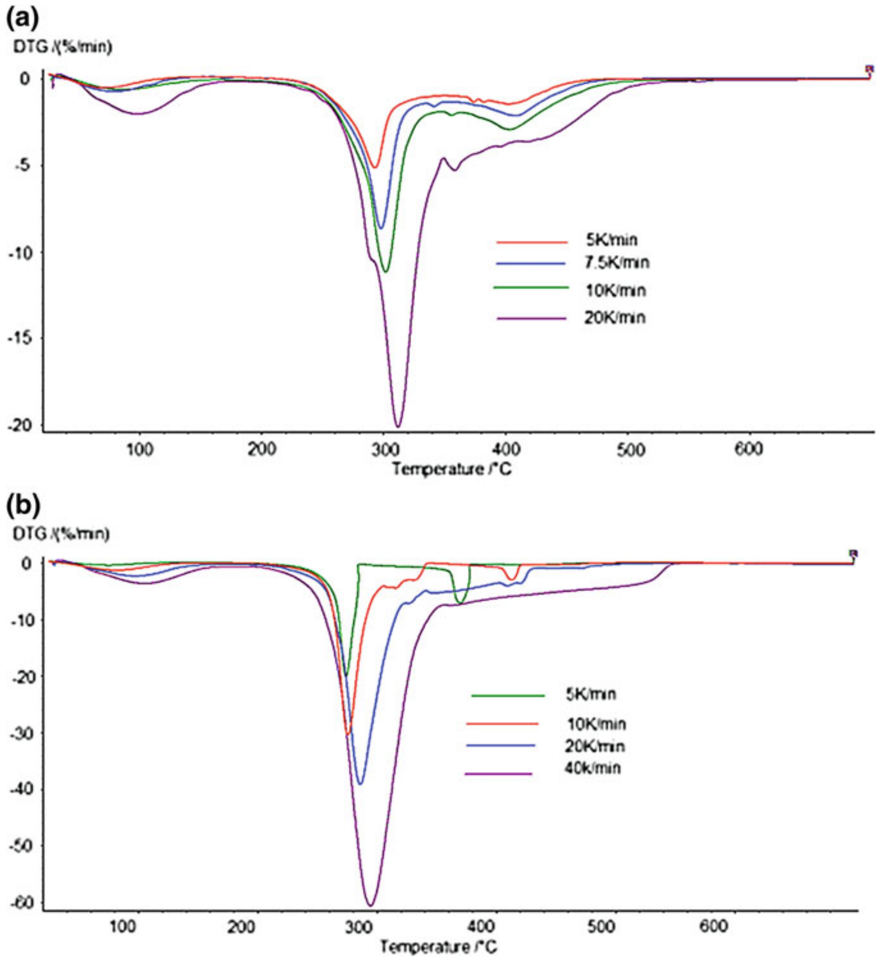

Fig. 32.3 **a** DTG of rice husks at various heating rates. **b** DTG of sisal pole at various heating rates. **c** DTG of Sugar bagasse at various heating rates. **d** DTG of coffee husks at various heating rate

Effect of these heating rates is shown in Fig. 32.3a and b. From this respect, it can be stated that the heating rate affects both location of the DTG curve and maximum decomposition rate.

According to the above mentioned DTG curves, the experimental data obtained, were processed in order to obtain kinetic parameters like the activation energy *E*, and pre-exponential factor *A*, as expressed in Table 32.2. From the set of DTG curves at different heating rates of each biomass, the T_{max} were obtained for calculation into Eq. (32.3) and the linear plot for slop determination is presented in Fig. 32.4. Because at higher temperature no significant changes in conversion occur from the biomass (Gašparovic et al. 2009).

Finding from other literatures available on establishing kinetic parameters for the studied tropical biomass are; Kinetic data obtained for mill bagasse 460.6 kJ/mol,

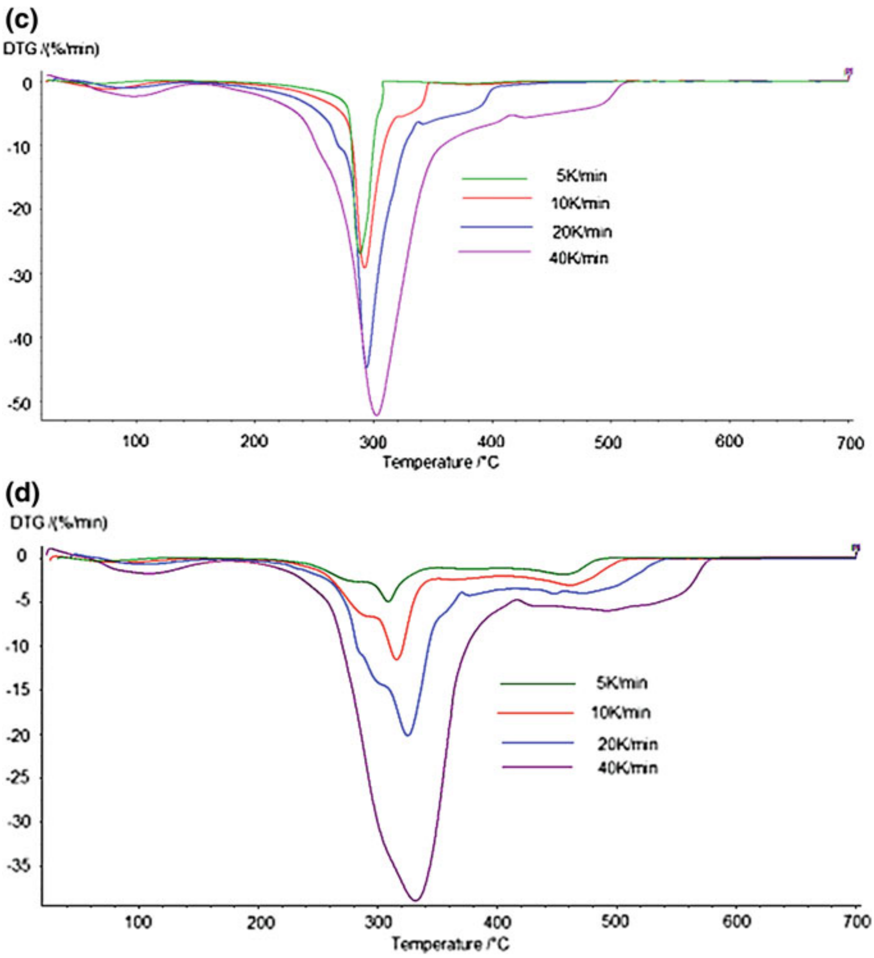

Fig. 32.3 continued

Table 32.2 Kinetic parameters of thermal decomposition of coffee husks, sugar bagasse, sisal pole and rice husks

	β (K/min)	E (kJ/mol)	A (/s)
Rice husks	5	268.98	5.28E+16
	7.5		
	10		
	20		
Sisal pole	5	267.81	2.91E+17
	10		
	20		
	40		
Sugar bagasse	5	533.11	1.62E+34
	10		
	20		
	40		
Coffee husks	5	297.05	1.14E+18
	10		
	20		
	40		

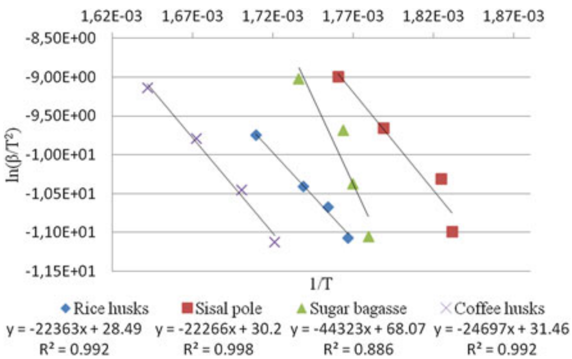

Fig. 32.4 Linear plot of $\ln(\beta/T_{max}^2)$ vs. $1/T_{max}$ at various heating rates for selected tropical biomasses

coffee husks 370.8 kJ/mol (Wilson et al. 2011). From this establish in respect of the method used by Ledakowicz and Stolarek (2002), the kinetic parameters obtained are 297.05, 533.11, 267.81 and 268.98 kJ/mol for coffee husks, sugar bagasse, sisal pole and rice husks respectively, for heating rates ranging from 5 to 40 K/min. The variability of the kinetic parameters is accepted on the bases of method used, originality and specific nature of the biomass materials under the study.

Conclusion

Selected tropical biomasses were successfully characterized. The proximate and ultimate analysis findings show that these materials have acceptable heating value with enough content of volatiles to be used as renewable energy sources, coffee husks highlighted with high energy content as per discussion. The content of nitrogen, sulphur, and chlorine is marginal in all biomasses.

- As regard to TGA analysis, the thermal decomposition of volatiles is mainly observed in the temperature range 240–500 °C for biomasses, where coffee husk is characterized with highest volatiles than others 88.7 %.
- From calculated kinetic parameters, is described that sugar bagasse has high values of activation energy 5.331 kJ/mol. The highest value of activation energy denotes the high temperature sensitivity of the charcoal formation reaction.

Therefore through these analyses results it is conforming that these biomasses are suitable for renewable energy source.

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