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Thermo-gravimetric characterization of biomass properties: A review

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Abstract. The performance of mathematical models, which can be used to predict the properties of biomass, depends on accurate characterization of feedstock and their thermal decomposition. So, the phenomenon of evaporation, decomposition and combustion that gives the specific energy embedded in the biomass are essential properties, which need to be thoroughly investigated. However, the experimental procedure for ultimate analysis and heating value requires equipment that is highly sophisticated, expensive, and demand a lot of time. Even at that, detailed information about the thermal decomposition of a biomass source may not be obtained through these procedures. Given this, a rapid and cost-effective method is inevitable for industrial scale biomass utilization. Thermogravimetry has proven over the years to be a technique, which can be used to characterize the properties of biomass rapidly and efficiently. This review article outlines the application, advantages and challenges with Thermogravimetry as related to biomass characterisation. The literature survey was carried out on state-of-the-art on biomass characterization using a thermo-gravimetric analytical method. In overall, the research gap in the current status of biomass characterization by the application of Thermogravimetry was highlighted. The effect of heating rate, gas flow rate, experimental atmosphere, nature of sample and particle size, are identified for future research.

1. Introduction

Biomass is the single naturally occurring energy source, which contains carbon resources in a large quantity such that it can be applied as a fossil fuel substitute [3, 4]. The characterization of biomass is an important aspect of biomass to energy process. To this extent, thermal analytical methods have found a wide and prominent application in recent years. The promising energy production via thermochemical conversion technologies, which comprise pyrolysis, gasification and combustion, depends on the thermal analysis in an actual qualification of the process [5, 6]. While the elemental composition and heating value are fundamental properties for biomass utilization, the thermal decomposition is required to accurately determine the characteristics and economic significance of various biomass samples and mixtures. The ultimate analysis requires unique instrumentation, while proximate analysis data can be sourced easily by using general equipment such as a furnace. It is expedient to understand the characteristics of biomass before it can be successfully explored for an industrial scale energy generation. Biomass from diverse sources has different properties [7]. Therefore, it may be costly to assume that all the biomass will behave the same way during utilization.



The properties of biomass include both physical and chemical phenomena which are: fusion, vaporization, sublimation, thermal decomposition, combustion, desorption, chemisorption, absorption, adsorption, transition temperature and oxidative stability [8-10]. Efficient and effective operation of bio-plant depends on the synchronization of the process parameters to the characteristics of feedstock's. The cost and time implication of biomass characterization based on ultimate analysis may not be practical for a rapid determination of the properties of biomass feedstock streaming into a processing plant [11]. Since these properties affect the conversion pathway, processing costs, yield and quality of products, an ability to rapidly estimate them for biomass feedstock streaming into a processing plant will be useful in the success and efficiency of bioconversion technologies [11]. The detailed understanding of solid volatilization dynamics would assist in the better planning of vital industrial processes since pyrolysis is not only an independent conversion technology but also part of the gasification and combustion processes [12]. Thermogravimetry (TG) is significant given the requirements mentioned above. Generally, the primary elements in biomass are: Carbon C, Oxygen O, Hydrogen H with lignin, Hemicellulose and cellulose as its main structural component [13]. TG is a branch of thermal analysis, which deals with the measurement of the mass change of samples. These measurements can be done as a function of changing temperature or isothermally as a function of time in an atmosphere of Nitrogen, Oxygen, Argon, Helium, Air, other gases, or vacuum [14]. By international standard, Thermogravimetry is defined as a method whereby the weight of substance under a controlled heating or cooling condition is recorded as a function of time or temperature [15]. The enormous need to develop a technique, which could accurately control the temperature and also provide a temperature versus time programme within a specific requirement, was the genesis of Thermogravimetry [16]. Thermo-gravimetric analysis (TGA) is a frequently used technique in the analysis of kinetic data [17].

Also, in a thermochemical process such as pyrolysis, an exhaustive knowledge of a biomass feedstock is important to the process design, feasibility, evaluation and scaling for industrial processes [13, 18]. The kinetic methods for the analysis of biomass and their relative advantages and disadvantages were discussed by Cai *et al.* [17]. They also establish from their search of the web of science that there is a growing trend in the research on the thermo-gravimetric analysis of biomass [17]. Their research highlighted the significance of Thermogravimetry in the study of biomass to energy conversion processes.

As the technology advances, several TGA models have emerged with different capability and several others can be used in conjunction with some measuring equipment such as Spectrometer, Infrared [9, 19, 20] and so on. TGA can be used as an effective tool to carry out the proximate analysis of solid fuels [21]. The main components of a TG analyser are: sample pan or crucible and furnace, balance, temperature measurement and control unit, environmental control unit, recording system [22, 23]. A precision balance supports the crucible. The crucible is placed in a furnace under a controlled heating condition and temperature. This implies that the physical and chemical properties of biomass, in this case, are continuously recorded. Thermal analysis involves several techniques, which are differentiated by the properties, which can be measured, though several of these properties can be measured at the same time. Figure 1 shows techniques and the properties, which can be measured. The performance of the TGA can be further enhanced to detect and identify the gas evolved from the sample in a time-space by Evolved gas analysis (EGA) based on mass spectroscopy and Infrared method [20, 24]. EGA is a method whereby the characteristics or the amount of gas given off from a material is detected as a function of controlled temperature. Indeed, characterisation of biomass using thermo-gravimetric analysis (TGA) and other thermal analytical technique has opened another page in the anal of biomass characterization. Table 1 shows different thermal analytical methods with the properties, which can be measured with the methods. Some of these methods can be combined to obtain more robust results.

Table 1: Thermal analysis technique and their measured properties[3]

S/N	Thermal analytical methods	Measured properties
-----	----------------------------	---------------------

1	Thermogravimetry (TGA)	analysis	It records the weight change at a controlled temperature.
2	Differential calorimetry (DSC)	scanning	Measure the heat difference between the sample and the reference.
3	Pressurized TGA (PTGA)		It records the mass changes as a function of a pressure.
4	Thermo-mechanical (TMA)	analysis	Deformations and dimension
5	Dilatometry (DIL)		Volume
6	Differential thermal analysis (DTA)	analysis	Temperature difference: It accounts for the temperature difference between the sample and the inert reference at a controlled temperature.
7	Evolved gas analysis (EGA)		Gaseous decomposition products
8	Combined methods		Can measure a combination of properties

The standard testing procedure was described in ASTM as follows[4]:

- ASTM Test Methods Using TG Analysis
- ASTM D2584 – Standard Test Method for Ignition Loss of Cured Reinforced Resins
- ASTM E1131 – Standard Test Method for Compositional Analysis by Thermogravimetry
- ASTM E1641 – Standard Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method
- ASTM E2008 – Standard Test Method for Volatility Rate by Thermogravimetry

1.1 Basic interpretation of TGA curves

Based on the shapes of the curve, TG can be classified into seven as shown in Table 2 [14, 27]. These classifications have been christened with different names depending on the research area and nature of the sample to which TG is applied [28, 29]. For instance, in the TG analysis of corn stover, which was conducted by Ajay et al. [2], three stages of thermal decomposition were identified. These are Dehydration stage, Active pyrolysis stage, and Passive pyrolysis stage.

Table 2: classification of TG based on the shapes of curves

Classification	Feature	Shape	Description
1	No change		The mass of a substance remains constant over the entire temperature range. This means the equipment temperature range is less than the cracking temperature of the substance.

2	Desorption/rerun		<p>Enormous weight loss followed by a mass plateau. In plateau, the mass is essentially constant. In the absence of reactive atmosphere in the chamber, the class 2 curve will change to class 1.</p>
3	Single stage cracking		<p>This curve typifies a single stage cracking with an initial temperature where a cumulative mass change reaches a detectable size for thermobalance and final temperature where the cumulative mass change reaches a maximum value.</p>
4	Multistage cracking		<p>Various reactions are resolved at this stage. The reaction interval is the temperature range between initial and final value.</p>
5	Unresolved multistage cracking.		<p>It is similar to a multistage cracking stage, but it may be due to rapid heating or absence of intermediate reaction.</p>
6	Atmospheric reaction		<p>Presence of reactive environment leads to increase in weight.</p>
7	Multiple reactions		<p>The atmospheric reaction followed by high-temperature decomposition of reaction product.</p>

2. Factors affecting the thermo-gravimetric analysis of Biomass

Several factors may affect the information, which could be obtained from TG; Experimental investigation of most of these factors have been previously reported in several studies [17, 30, 31]. These factors to a greater or less extent may influence the shape, reproducibility or correctness of thermo-gravimetric curve for a particular compound or mixture [30]. Changing the experimental conditions may significantly affect the product obtained in TGA [32]. These factors need to be kept in mind to accomplish a reproducible TGA result [10, 33, 34]. They are at this moment briefly discussed:

2.1. Heating rate

The heating rate can be defined as the rate at which the temperature increases in degrees per minute based on the Celsius or Kelvin temperature scale. If the temperature or time curve of a sample is linear, then the heating or cooling rate is said to be constant [35]. The heating rate is an instrumental factor, and it has a severe effect on the pyrolysis process. Newkirk [36] has proved that when a sample is heated at a slower rate, the extent of decomposition is more significant than when it is heated at a higher rate at any given temperature. The rate at which the sample is heated is very vital when considering a case of slow or complex reactions. Fast heating rates shift the reactions to higher temperatures [37]. The importance of heating rate has triggered several researchers to investigate its effect on the dynamics of various biomasses [8, 33, 38-40]. For instance, the products of pyrolysis are gases, liquid and solid. But, when the temperature and the heating conditions are changed, the nature of the products, which can be obtained, is changed. At the low heating temperature and heating rate, maximum solid formation is achieved, but high temperature and heating rate yields maximum gas formation. Increasing the heating rate and gas flow promoted the thermal decomposition in a corncob and also increase loss in weight [33], but a proportionate amount of solid, gas and liquid are obtained at intermediate temperature and heating rates [41].

2.2. Type of Sample and sizes

It has been established that some materials show changes in composition and crystal structure after fine grinding [37]. A particle with a low ratio of surface area to weight will react more slowly when compared with a biomass sample of equal mass but of finer particle size. Particle size distribution and packing density are not very easy to reproduce. Therefore, particular attention must be paid to their investigation. [10]. Particle size can be a vital parameter, which may influence the process rate. Generally, it has been suggested that an increase in particle size causes temperature gradients inside the particle such that at a given time the core temperature is lower than that at the surface [42]. Some researchers have also proven that the particle size does not have significant influence within certain particle diameter [32, 42, 43]. Effect of particle size was investigated by Erika *et al.* [44]. They observed that grinding of some energy crops resulted in higher peak maxima [44] and they equally advised that only particles of equal sizes should be compared in relation to thermal characteristics. There are three ways in which the thermo-gravimetric curve can be influenced with regards to sample size. The weight of the sample will cause the temperature to deviate from its linear rise, the degree of diffusion through the pores around the solid particles will be somewhat governed by the bulk of the material in the crucible and the likelihood of uneven temperature distribution in the sample [12, 32, 33, 45].

A TGA method was applied to various materials prepared from commercially available Refuse Derived Fuel, RDF using a variety of procedures. Applicability of TGA method to the determination of the renewable content of RDF was considered. Cryogenic ball milling was found to be an effective means of preparing RDF samples for TGA [45] Also, it was advised that a small weight and uniform biomass sample should be considered to mitigate the effects such as non-uniform temperature distribution, product decomposition and so on [37]. Other properties such as thermal conductivity, thermal capacity, packing density of particles, sample expansion and shrinking, sample mass, crystal structure [46] affect the characteristics of biomass samples.

2.3. Experimental Atmosphere

The nature and the pressure at the environment of a sample have a notable effect on the decomposition temperature of a biomass [30, 37, 45]. The atmosphere may or may not take part in a reaction. In the case where the atmosphere does not take part in the reaction, the inert gas such as nitrogen is used to remove the gaseous products from the vicinity of a sample [10, 47]. This will ensure that the experimental atmosphere is kept constant as possible throughout the process and to prevent a reaction between the biomass sample and air [10]. In some other cases, the atmosphere may be considered in the process [10, 12, 37, 44]. The comparative study of the effect of the atmosphere on the thermal properties of biomass has been carried out by some researchers, which include [12, 34, 44, 48, 49]. The steepness of a TG slope was shown to be affected by the experimental environment [33].

2.4. Gas flow rate

At the pyrolysis reaction zone, the resident time of gaseous products is intimately related to the carrier gas flow rate [50]. Therefore, the residence time of a product decreases with an increase in gas flow. Gaseous products released from the pyrolytic process could be streamed away from the pyrolytic region at a high gas flow rate, thereby accelerating the thermal cracking of biomass [33]. Also, in a gas phase of pyrolysis, a certain threshold of the gas flow rate may be enough to mitigate the potential differences, which could be the consequence of external heat and mass transfer [43].

All the factors which have been discussed above were investigated by Yao et al. [33] for a corncob. While they reported that the gas flow rate does not have any significant effect on the thermal decomposition, they asserted the prominent role of heating rate on the thermal decomposition and also underline the significance of particle size which is only within a certain threshold of particle diameter [33]. However, the effect of blending and contamination was not investigated, since it was not within the scope of their article.

3. Merits of Thermogravimetric analysis of biomass

TGA has proven to be very important in a lot of analytical processes, which also include biomass characterization. The merits of TGA are outlined below [5-8].

- It requires less time and expenses.
- A relatively small dataset is required.
- The weight loss is progressively recorded as a function of time or temperature. This ensures the uniformity of the procedure over the entire study.
- The various kinds of kinetic parameters are clearly indicated since a single sample is analysed over the entire temperature range.
- It can be used in the analysis of all sort of solids including biomass with minimum procedure in sample preparation.
- It requires minimum sample size.
- It can be easily implemented.
- It gives good repeatability.

4. Thermogravimetric analysis of biomass.

4.1. Thermal stability

It can be defined as the ability of a substance to maintain unchanged properties when subjected to heating [14, 53]. Thermal stability means there is no apparent weight loss at the temperature under investigation, and this gives an indication of the amount of the volatile content in the biomass sample. A thermally stable biomass sample has less volatile matter. Also, maximum temperature limit is an indication of the point at which a biomass material begins to decompose [29, 54, 55]. The information about thermal stability is significant for engineers as they can determine the temperature or temperature ranges at which substances like alloy, building materials, polymers, biomass fibres, etc. can be used [14, 29]. Materials that are related can be compared at elevated temperatures under the required atmosphere.

Matheus *et al.* [56] compared the thermal stability and activation energy of sawdust of different wood species. Thermal stability of biomass samples can be affected by the experimental environment [49]. Chiang *et al.* [49] observed that the oxygen environment speeded up the thermal degradation of rice husk from 600 K, till the end of the decomposition process. Just like polymers, the rate of decomposition of biomass determines the thermal stability of a sample.

4.2. Oxidative stability analysis

Oxidative stability is a critical issue that affects the commercial utilization of bioenergy. In the automobile sector, the oxidative stability is a hugely significant characteristic which provides an estimate of the storage life of biodiesel [57]. Several authors have investigated the oxidative stability of biomass [57-60]. Some of the factors which affect the oxidative stability are; Structures, external conditions, storage material or impurities. Kumar [57] highlighted the effects of oxidized biodiesel as follows; Inability to provide lubrication [58], lower CO emission and higher NO_x emission, and change in quality. When a fuel product is degraded by oxidation, the quality of the fuel products that are yielded may be impaired and may retard engine efficiency [61]. While oxidative stability could be a disadvantage in some biomass application, it has been found to be of help in some others [57, 58]. Therefore, the effect of oxidative stability can be investigated by TGA. Weight losses due to oxidation are the most noticeable losses in TGA [62]. Combustion during TG analysis is identifiable by distinct effects noticeable on the TGA thermo-grams generated. As an example, Okoroigwe *et al.* [60] investigated the oxidation characteristics of some selected biomass of African origin which are palm kernel shell, African bush mango wood, and shell, African border tree wood to underline the combustion characteristics and decomposition kinetics of biomass under oxidative conditions. It was reported that all the samples followed two stages structural decomposition with the most significant weight loss occurring at an oxidation stage in all the samples.

4.3. Compositional analysis

The traditional compositional analysis tool such as ultimate analysis is time-consuming and cost ineffective as such they may not meet the immediate demand for industries which are time and profit driven. Therefore, TG could provide a quick rapid [11] measuring technique. In the process of thermal decomposition, and with a careful selection of temperature programming and experimental environment, contaminated biomass or mixtures may be analysed by decomposing or removing their components [63].

5. Applications of Thermogravimetry Analysis

- TGA can be used in the characterization of materials through the evaluation of degradation pattern and formulation of reaction kinetics[9]. The knowledge of the controlling chemistry or predictive studies would give room to different kinds of techniques which can be used to evaluate the kinetics of weight loss or gain.
- In TGA method for proximate analysis, the moisture content, volatile matter, Ash content and fixed carbon content are determined[10]. These parameters can be obtained from the weight loss over time.
- By careful choices of temperature and experimental environment, the composition of complex mixture can be analysed through decomposition TGA can quantitatively resolve complex mixtures because of the characteristic thermal decomposition temperature of each component [11][18][12, 13].
- The structural components of a biomass such as a hemicellulose and alpha cellulose can be characterised by TG[14].
- Investigation of pyrolysis, combustion and Devolatilization processes which are involved in the conversion of biomass and blends to energy.[15, 16].TGA can be coupled to a spectrometer for improving the understanding of the thermal decomposition mechanisms and to estimate the amounts of biogas - such as methane and hydrogen - produced during the pyrolytic process [17, 18][16,17].

- TGA can be used as a quick assessment tool for waste management [19] while also serving as a crucial tool for providing information on the thermal and kinetic behaviour of biomass for the energy recovery and the utilization of sewage sludge, thereby reducing the possible environmental impact[20].
- TGA may be used to determining water content or the residual solvents in a material.
- It allows analysis of reactions with air, oxygen, or other reactive gases. It can be used to measure evaporation rates as a function of temperature, such as to measure the volatile emissions of liquid mixtures. To identify plastics and organic materials by measuring the temperature of bond scissions in inert atmospheres or of oxidation in air or oxygen.

6. Heating conditions in TGA [3]

In TGA analysis, the biomass weight loss is in different stages depending on the heating conditions of biomass samples. These stages are also affected by the intrinsic properties of the biomass sample [1, 33]. Figure 1 is an example of TGA curve indicating the effect of gas flow rate and heating rate on the mass fraction. The heating conditions in TGA can be broadly classified into three [25]. They are briefly described below.

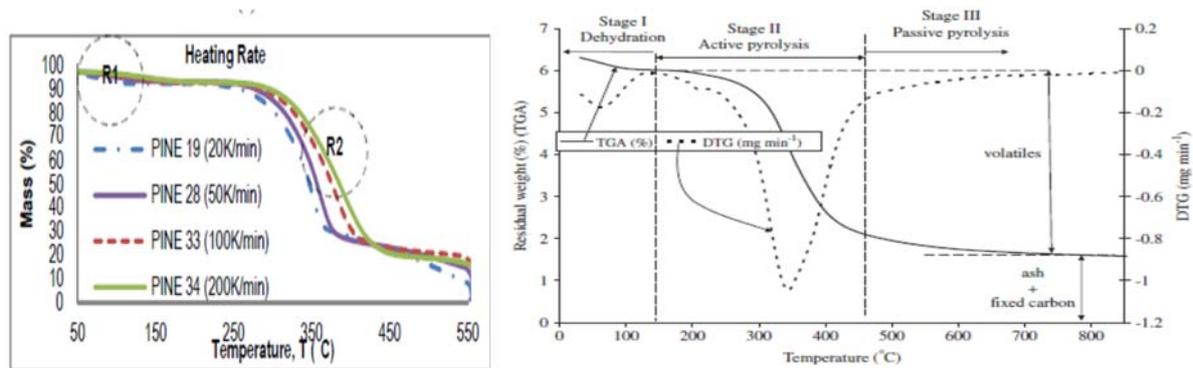


Figure 1: Weight loss versus temperature at different gas flow rates [1, 2]

6.1. Isothermal or Static TGA

In this case, a sample is maintained at a constant temperature for a period during which change in weight is recorded [25]. The conversion time is the sole variable of interest in several cases. For example, in thermochemical conversion of wood [27]. In fact, given the thick particles and slow external heat transfer rates, devolatilization conditions are comparable with those of thermal analysis and the corresponding product yields remain almost constant.

6.2. Quasi-static TGA

Quasi-static process can be briefly described as a process that occurs in a slow manner such that the system can be assumed to remain in internal equilibrium. In this technique, the sample is heated to a constant weight at each of a series of increasing temperature [14].

6.3. Dynamic TGA

It is also called isobaric TGA. In this type of analysis, the sample is subjected to a condition of a continuous increase in temperature at a constant heating rate. Therefore, the rise in temperature shows a linear relationship with time [33].

7. Basic principles of thermogravimetric analysis

Thermogravimetry analyser measures the change in weight of a sample depending on time or temperature in a given environment which could be inert or oxidative [53] and at a controlled rate. Chemical changes occurring in an oxidative atmosphere provide useful information regarding

characterization of the sample. The weight variation of samples is recorded as a function of temperature or time. Depending on the heating condition, the heating rate or gas flow is varied while temperature changes at a constant rate for a known initial mass of the substance and the variation in mass are recorded as a function of temperature within a specified time interval. The graphical representation of the mass change versus time is known as thermography [9]. For some types of TGA, gas flow into the furnace atmosphere is controlled by a computer-based program. Different setting is available for different types of analysis [19, 23].

8. Matter arising from thermogravimetric analysis of biomass.

8.1. Uncertainty analysis of biomass thermal properties.

Statistical analysis of the sampling error or uncertainty associated with the sampling and properties measured in a TG analysis is very crucial in an application where precision is important [71]. Also, uncertainty analysis could help in determining the propagation of error in the sampling procedure [71-73]. Although biomass fuels are heterogeneous materials, with an appropriate sampling procedure, the experimental error associated with different properties, can be considerably sized down. Pazo *et al.* [74] show that sample variance cannot accurately quantify error levels. The statistical uncertainty associated with this property needs to be determined for errors to be quantified precisely. It can be concluded that a well-planned sampling and uncertainty analysis can assist in the extrapolation of the biomass properties notwithstanding their non-uniformity [73].

8.2. Previous research on the thermogravimetry

The characteristics of several biomass samples have been investigated for various purposes such as combustion, thermochemical conversion [2, 8, 9, 20, 24, 28, 29, 38, 48, 75]. Table 3 shows some biomass resources, which have been investigated to establish their thermal characteristics under the different experimental conditions that apply to TGA. The variables which were commonly investigated in this review are; the experimental atmosphere, the heating rate, the particle size, heating condition, gas flow rate and the uncertainties in biomass sampling and thermal properties obtained from TGA.

Table 3: Experimental characterisation of Biomass by TGA

Author	Biomass sample	Particle size[μ m]	Experimental atmosphere	Heating rate[K/min]	Heating conditions	Gas flow rate[cm ³ /min]	Properties investigated	Temperature(K)		Uncertainties and error
								Ignition	Burn out	
[16]	Feedlot manure	420-840	Dry Nitrogen	40 and 160	Dynamics	50 and 150	Devolatization	-	-	Not discussed
[21]	Swine manure	1000	Nitrogen	20,30,40	Dynamics and Isothermal	30	Devolatization	250	420	Not discussed
			Nitrogen	105						
[22]	Hazelnut	<250	Air	10,20,30	Dynamics	50	Reaction region and kinetics	350,371,395	443,458,498	No discussed
[23]	Primary mill sludge	105-210	Oxygen	6,12,24,30	Dynamics	100	Combustion	479,481,487,490	1009,1034,1067,1077	Not discussed
	Secondary mill sludge	105-210	Oxygen	6,12,24,30	Dynamics	100	Combustion	465.475,480,485	975,995,1030,1030	Not discussed
[15]	Miscanthus	200-400	Oxygen	40	Dynamics	2	Combustion	230	330	Not discussed
	Miscanthus	200-400	Argon	40	Dynamics	20	Pyrolysis	250	370	Not discussed
	Miscanthus	200-400	steam	40	Dynamics	6g/h	Pyrolysis	815	1000	Not discussed
	Miscanthus	200-400	Steam+Oxygen +Air	40	Dynamics	50	Gasification	800	900	Not discussed
	Sewage sludge	100	Steam+Oxygen +Air	40	Dynamics	50	Gasification	800	940	Not discussed
	Sewage Sludge	100	Oxygen	40	Dynamics	2	Combustion	200	310	Not discussed

	Sewage +Sludge	100	Steam	40	Dynami c	6kg/h	Gasification	800	940	Not discussed
	Sewage	100	Argon	40	Dynami c	20	Pyrolysis	220	375	Not discussed
[8]	Cypress wood chips	250-350	Air	5,10,15,20	Dynami c	20	Combustion	200	334	Only R ² was stated
	Macadamia nut shells	250-350	Air	5,10,15,20	Dynami c	20	Combustion	200	328	Only R ² was stated
[24]	Pine nut shells	30	Nitrogen	0.001-50	Isotherm al	45	Combustion	-	-	0.721
	Hazelnut shells				Isotherm al	45	Combustion			
	Poplar pellets									
[25]	Brassica pellet	440-2000	Nitrogen	Not stated	Isotherm al	200	Pyrolysis	-	-	Not discussed
	Olive Grape bagasse									
[26]	Palm oils shell waste	150-850	Nitrogen	0.1-20	Isotherm al	40-120	Pyrolysis	230,250,260,280,290,295	280,300,310,330,350,350	Coefficient of correlation was determined at maximum value of 0.9969
	Palm oil fibre waste	125-150								
	Empty fruit bunches	125-1000								
[13]	Napier grass	200-2000	Nitrogen	10	Isotherm al	20	Pyrolysis	478	600	R ² =0.988-0.996
[27]	Eucalyptus grandis		Nitrogen Air	10	Isotherm al	50		160 105	374 540	Not given
[28]	Tectona grandis	420-4000	Nitrogen	20	Isotherm al	100	Combustion	250	400	Not given
[1]	Pine	-	Nitrogen	20-200	Dynami cs	20-50	Pyrolysis	-	-	Not discussed
[29]	Bamboo		Nitrogen	20,100,200	Isotherm al and adiabati c	20	Pyrolysis	250	400	Not discussed
[30]	alder Beech Birch Oak	-	Nitrogen	5-30	Isotherm al	150	Devolatilizat ion	515 521 517 510	644 645 645 633	Not discussed
[31]	Rice husk	-	Air Nitrogen	10	Isotherm al	50	Thermal decompositi on	230 230	540 380	Not discussed
[32]	Rice straw	-	Nitrogen, 10% Oxygen and Air	2,5,10	Isotherm al	70	Thermal decompositi on	450	640	Not discussed
[33]	Black locust	≤120	Oxygen-argon mixture (5:21)	20	Isotherm al	140	Thermal decompositi on	249	372	Not discussed
[20]	Sewage sludge and mixture		Nitrogen	10,20,30	Isotherm al	100	Thermal decompositi on	250	360	Not discussed
[34]	MSW (Plastic, cardboard, wood, plastic, multi-material)	-	Nitrogen	10	isotherm al	150	Pyrolysis of mixture	250-370	325-550	Not discussed
[35]	Pine wood	595-841	Nitrogen	5,10,20,40		50		210	400	Not discussed
[2]	Corn Stover	443	Nitrogen Air	10,30,50	Isotherm al	40	Pyrolysis	110,135,140 115,135,130	420,435,470 400,410,430	Not discussed
[36]	Corncob	74-450	Helium	5,10,20	Dynami cs	10	Influence of heating rate	100	600	R ² =0.99
				30	Isotherm al	30,60,90	Influence of gas flow	177.2	347.6	R ² =0.98-0.99
				20		30	Influence of particle diameter	175.2-182.5	352.6-360.2	R ² =0.98-0.99

8.3. Future Outlook

As previously highlighted by these authors, a detailed understanding of the contribution of biomass utilization to the emission of Green House Gas (GHG) is very vital. Therefore, TGA can help in this regard. Although the contribution of biomass samples to GHG may not be significant at the experimental level, the cumulative impact of this may be so substantial in the case of industrial utilization.

Also, only a few journals reported the uncertainties of their thermal analysis and sampling methods, and this may call the reliability of the result to question. Therefore, it is suggested that the uncertainty analysis should be included in the thermal analytical results. In all biomass analysis, sample error should be made to be part of the standard experimental procedure.

The evaluation of thermal behaviour as well as kinetic studies of the decomposition of biomass and its mixture can give a better insight into the biomass energy utilization while opening a new frontier on environmental issues. Further investigation is still needed on the thermo-gravimetric analysis of biomass mixture and contaminated biomass since their thermal decomposition, and other characteristics which are investigated by TGA may not behave in the same manner as a single component sample. The factors, such as; the particle size, heating rate, gas flow rate, the experimental atmosphere should be investigated for biomass mixture, this would provide more robust information on the combustion characteristics of the samples and also validate few existing results on biomass mixtures.

9. Conclusion

The enormous information, which can be obtained from TGA would provide a fast, accurate and efficient means to determine the utilization of a biomass sample or mixture. TGA has been used in combination with other analytical methods, and this has enhanced the understanding of biomass properties. The uncertainty analysis of a biomass sample is very vital in industrial application. Also, more detailed knowledge of the characteristics of contaminated biomass and biomass mixture using TGA is very crucial. These would eventually lead to a robust modelling tool, which can be used to determine the utilization of biomass irrespective of nature.

References

- [1]A. Abu-Bakar and K. Moinuddin, "Effects of variation in heating rate, sample mass and nitrogen flow on chemical kinetics for pyrolysis," in 18th Australasian fluid mechanics conference Launceston, Australia, 2012, pp. 3-7.
- [2]A. Kumar, L. Wang, Y. A. Dzenis, D. D. Jones, and M. A. Hanna, "Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock," *Biomass and Bioenergy*, vol. 32, no. 5, pp. 460-467, 2008.
- [3]M. Balat and G. Ayar, "Biomass energy in the world, use of biomass and potential trends," *Energy sources*, vol. 27, no. 10, pp. 931-940, 2005.
- [4]K. A. Motghare, A. P. Rathod, K. L. Wasewar, and N. K. Labhsetwar, "Comparative study of different waste biomass for energy application," *Waste Manag*, vol. 47, no. Pt A, pp. 40-5, Jan 2016.
- [5]A. V. Bridgwater, "Renewable fuels and chemicals by thermal processing of biomass," *Chemical Engineering Journal*, vol. 91, no. 2-3, pp. 87-102, 2003.
- [6]L. Zhang, C. C. Xu, and P. Champagne, "Overview of recent advances in thermo-chemical conversion of biomass," *Energy Conversion and Management*, vol. 51, no. 5, pp. 969-982, 2010.
- [7]S. V. Vassilev, D. Baxter, L. K. Andersen, and C. G. Vassileva, "An overview of the chemical composition of biomass," *Fuel*, vol. 89, no. 5, pp. 913-933, 2010.
- [8]J. Chen et al., "Investigation of co-combustion characteristics of sewage sludge and coffee grounds mixtures using thermogravimetric analysis coupled to artificial neural networks modeling," *Bioresour Technol*, vol. 225, pp. 234-245, Feb 2017.
- [9]A. M. Evaluation, "TGA Analysis or Thermogravimetric Analysis," <http://www.andersonmaterials.com/tga.html> accessed on 28th April, 2018, 2018.
- [10]A. Coats and J. Redfern, "Thermogravimetric analysis. A review," *Analyst*, vol. 88, no. 1053, pp. 906-924, 1963.

- [11]G. E. Acquah, B. K. Via, O. O. Fasina, S. Adhikari, N. Billor, and L. G. Eckhardt, "Chemometric modeling of thermogravimetric data for the compositional analysis of forest biomass," *PLoS One*, vol. 12, no. 3, p. e0172999, 2017.
- [12]M. G. Grønli, G. Várhegyi, and C. Di Blasi, "Thermogravimetric analysis and devolatilization kinetics of wood," *Industrial & Engineering Chemistry Research*, vol. 41, no. 17, pp. 4201-4208, 2002.
- [13]V. Dhyani and T. Bhaskar, "A comprehensive review on the pyrolysis of lignocellulosic biomass," *Renewable Energy*, 2017.
- [14]NPTEL, "Thermogravimetric analysis," <http://nptel.ac.in/courses/115103030/21> accessed on 29th April, 2018, 2016.
- [15]R. Mackenzie, "Note," *Talanta*, vol. 16, no. 8, pp. 1227-1230, 1969.
- [16]C. Keattch, "Studies in the history and development of thermogravimetry," *Journal of thermal analysis*, vol. 44, no. 5, pp. 1211-1218, 1995.
- [17]J. Cai et al., "Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk," *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 2705-2715, 2018.
- [18]S. Wang, G. Dai, H. Yang, and Z. Luo, "Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review," *Progress in Energy and Combustion Science*, vol. 62, pp. 33-86, 2017.
- [19]E. A. G. LLC, "Thermogravimetric analysis (tga)/differential thermal analysis (dta)." http://www.eaglabs.com/techniques/analytical_techniques/tga_dta.php(accessed on 30th April 2018, 2011).
- [20]S. Singh, C. Wu, and P. T. Williams, "Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques," *Journal of Analytical and Applied Pyrolysis*, vol. 94, pp. 99-107, 2012.
- [21]J. Cai et al., "Review of physicochemical properties and analytical characterization of lignocellulosic biomass," *Renewable and Sustainable Energy Reviews*, vol. 76, pp. 309-322, 2017.
- [22]M. E. Brown and P. K. Gallagher, *Handbook of thermal analysis and calorimetry: recent advances, techniques and applications*. Elsevier, 2011.
- [23]P. t. Edulab, "Thermogravimetry," <https://www.pharmatutor.org/articles/thermogravimetry> accessed on 12th May,2018, 2018.
- [24]A. E2105-00, "Standard practice for general techniques of Thermogravimetric Analysis (TGA) coupled with Infrared Analysis (TGA/IR). West Conshohocken, PA," ASTM International, 2016.
- [25]N. S, "Thermal Methods of Analysis. Mod Appl Pharm Pharmacol. 1(2). MAPP.000509. ," 2017.
- [26]ASTM, "Standard test methods," <https://www.astm.org> accessed on 30th April, 2018, 2017.
- [27]N. Vhathvarothai, J. Ness, and Q. J. Yu, "An investigation of thermal behaviour of biomass and coal during copyrolysis using thermogravimetric analysis," *International journal of energy research*, vol. 38, no. 9, pp. 1145-1154, 2014.
- [28]N. P. Makaringe, I. I. Van der Walt, G. J. Puts, and P. L. Crouse, "TGA-FTIR characterisation of bamboo wood, napier grass, pine wood and peach pips for gasification applications."
- [29]X. Liu and W. Yu, "Evaluating the thermal stability of high performance fibers by TGA," *Journal of applied polymer science*, vol. 99, no. 3, pp. 937-944, 2006.
- [30]A. Berlin and R. J. Robinson, "Thermogravimetric analysis: temperature limits and rate of heating," *Analytica Chimica Acta*, vol. 27, pp. 50-57, 1962.
- [31]A. G. Barneto, J. A. CArmona, and J. A. Conesa, "Effects of the composting and the heating rate on biomass gasification," *Energy & Fuels*, vol. 23, no. 2, pp. 951-957, 2008.
- [32]J. Encinar, F. Beltran, A. Bernalte, A. Ramiro, and J. Gonzalez, "Pyrolysis of two agricultural residues: olive and grape bagasse. Influence of particle size and temperature," *Biomass and Bioenergy*, vol. 11, no. 5, pp. 397-409, 1996.
- [33]X. Yao, K. Xu, and Y. Liang, "Assessing the Effects of Different Process Parameters on the Pyrolysis Behaviors and Thermal Dynamics of Corncob Fractions," *BioResources*, vol. 12, no. 2, pp. 2748-2767, 2017.

- [34]I. Abed, M. Paraschiv, K. Loubar, F. Zagrouba, and M. Tazerout, "Thermogravimetric investigation and thermal conversion kinetics of typical North-Africa and middle-east lignocellulosic wastes," *BioResources*, vol. 7, no. 1, pp. 1120-1220, 2012.
- [35]A. compedium, "http://old.iupac.org/publications/analytical_compedium/Cha05sec2.pdf accessed on 10th May, 2018," IUPAC, 2002.
- [36]A. E. Newkirk, "Thermogravimetric measurements," *Analytical Chemistry*, vol. 32, no. 12, pp. 1558-1563, 1960.
- [37]H.-G. Wiedemann and G. Bayer, "Trends and applications of thermogravimetry," in *Inorganic and Physical Chemistry*: Springer, 1978, pp. 67-140.
- [38]I. Boumanchar et al., "Effect of materials mixture on the higher heating value: Case of biomass, biochar and municipal solid waste," *Waste Manag*, vol. 61, pp. 78-86, Mar 2017.
- [39]A. Kakitis, I. Nulle, M. Ozollapins, and J. Kjakste, "Assessment of combustion parameters of biomass mixtures," in *14th International Scientific Conference Engineering for Rural Development*, Jelgava, Latvia, 20-22 May, 2015, 2015, pp. 133-139: Latvia University of Agriculture.
- [40]R. Zanzi, K. Sjöström, and E. Björnbom, "Rapid high-temperature pyrolysis of biomass in a free-fall reactor," *Fuel*, vol. 75, no. 5, pp. 545-550, 1996/04/01/ 1996.
- [41]T. Abbasi and S. A. Abbasi, "Biomass energy and the environmental impacts associated with its production and utilization," *Renewable and Sustainable Energy Reviews*, vol. 14, no. 3, pp. 919-937, 2010.
- [42]W. C. R. Chan, M. Kelbon, and B. Krieger-Brockett, "Single-particle biomass pyrolysis: correlations of reaction products with process conditions," *Industrial & engineering chemistry research*, vol. 27, no. 12, pp. 2261-2275, 1988.
- [43]H. Yang, R. Yan, T. Chin, D. T. Liang, H. Chen, and C. Zheng, "Thermogravimetric analysis–Fourier transform infrared analysis of palm oil waste pyrolysis," *Energy & fuels*, vol. 18, no. 6, pp. 1814-1821, 2004.
- [44]E. Mészáros, G. Várhegyi, E. Jakab, and B. Marosvölgyi, "Thermogravimetric and reaction kinetic analysis of biomass samples from an energy plantation," *Energy & Fuels*, vol. 18, no. 2, pp. 497-507, 2004.
- [45]T. Robinson, B. Bronson, P. Gogolek, and P. Mehrani, "Sample preparation for thermo-gravimetric determination and thermo-gravimetric characterization of refuse derived fuel," *Waste Management*, vol. 48, pp. 265-274, 2016.
- [46]P. J. Haines, *Thermal methods of analysis: principles, applications and problems*. Springer Science & Business Media, 2012.
- [47]J. Soulen and I. Mockrin, "Improved methods of using the thermobalance to determine thermal stabilities," *Analytical Chemistry*, vol. 33, no. 13, pp. 1909-1911, 1961.
- [48]C.-Y. Yin and B.-M. Goh, "Thermal degradation of rice husks in air and nitrogen: thermogravimetric and kinetic analyses," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 34, no. 3, pp. 246-252, 2011.
- [49]W.-F. Chiang et al., "The effect of oxygen on the kinetics of the thermal degradation for rice straw," *Journal of the Air & Waste Management Association*, vol. 59, no. 2, pp. 148-154, 2009.
- [50]D. Ferdous, A. Dalai, S. Bej, R. Thring, and N. Bakhshi, "Production of H₂ and medium Btu gas via pyrolysis of lignins in a fixed-bed reactor," *Fuel Processing Technology*, vol. 70, no. 1, pp. 9-26, 2001.
- [51]T. Hatakeyama and F. Quinn, *Thermal analysis: fundamentals and applications to polymer science*. [sl], 1999.
- [52]D. L. Klass, *Biomass for renewable energy, fuels, and chemicals*. Elsevier, 1998.
- [53]N.-G. GmbH, "Thermogravimetric Analysis – TGA:Method, Technique, Applications," <https://www.netzsch-thermal-analysis.com/en/> accessed on 29th April, 2018, 2012.

- [54]T. Zhang, J. Jin, S. Yang, D. Hu, G. Li, and J. Jiang, "Synthesis and characterization of fluorinated PBO with high thermal stability and low dielectric constant," *Journal of Macromolecular Science, Part B*, vol. 48, no. 6, pp. 1114-1124, 2009.
- [55]C. S. Marvel, "Synthesis of Thermally Stable Polymers," ARIZONA UNIV TUCSON1972.
- [56]M. Poletto, J. Dettenborn, V. Pistor, M. Zeni, and A. J. Zattera, "Materials produced from plant biomass: Part I: evaluation of thermal stability and pyrolysis of wood," *Materials Research*, vol. 13, no. 3, pp. 375-379, 2010.
- [57]N. Kumar, "Oxidative stability of biodiesel: Causes, effects and prevention," *Fuel*, vol. 190, pp. 328-350, 2017/02/15/ 2017.
- [58]R. Kreivaitis, J. Padgurskas, M. Gumbytė, V. Makarevičienė, and B. Spruogis, "The influence of oxidation on tribological properties of rapeseed oil," *Transport*, vol. 26, no. 2, pp. 121-127, 2011.
- [59]K. A. Sorate and P. V. Bhale, "Biodiesel properties and automotive system compatibility issues," *Renewable and Sustainable Energy Reviews*, vol. 41, pp. 777-798, 2015.
- [60]E. C. Okoroigwe, S. Enibe, and S. Onyegegbu, "Determination of oxidation characteristics and decomposition kinetics of some Nigerian biomass," *Journal of Energy in Southern Africa*, vol. 27, no. 3, pp. 39-49, 2016.
- [61]J. Pullen and K. Saeed, "An overview of biodiesel oxidation stability," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 8, pp. 5924-5950, 2012.
- [62]V. Voitovich, V. Lavrenko, R. Voitovich, and E. Golovko, "The effect of purity on high-temperature oxidation of zirconium," *Oxidation of metals*, vol. 42, no. 3-4, pp. 223-237, 1994.
- [63]C. E. M. Braz and P. C. G. M. Crnkovic, "Physical-chemical characterization of biomass samples for application in pyrolysis process," *Chemical Engineering Transactions*, pp. 523-528, 2014.
- [64]I. Mohammed, Y. Abakr, F. Kazi, S. Yusup, I. Alshareef, and S. Chin, "Comprehensive characterization of napier grass as a feedstock for thermochemical conversion. *Energies*, 8 (5), 3403-3417," ed, 2015.
- [65]M. Carrier et al., "Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass," *Biomass and Bioenergy*, vol. 35, no. 1, pp. 298-307, 2011.
- [66]K. Jayaraman and I. Gökalp, "Pyrolysis, combustion and gasification characteristics of miscanthus and sewage sludge," *Energy Conversion and Management*, vol. 89, pp. 83-91, 2015.
- [67]P. Raman, W. P. Walawender, L. Fan, and J. A. Howell, "Thermogravimetric analysis of biomass. Devolatilization studies on feedlot manure," *Industrial & Engineering Chemistry Process Design and Development*, vol. 20, no. 4, pp. 630-636, 1981.
- [68]G. Varhegyi, E. Jakab, F. Till, and T. Szekely, "Thermogravimetric-mass spectrometric characterization of the thermal decomposition of sunflower stem," *Energy & fuels*, vol. 3, no. 6, pp. 755-760, 1989.
- [69]E. Mészáros, E. Jakab, G. Várhegyi, and P. Tóvári, "Thermogravimetry/mass spectrometry analysis of energy crops," *Journal of thermal analysis and calorimetry*, vol. 88, no. 2, p. 477, 2007.
- [70]W. Nozela, C. Braz, S. Almeida, C. Ribeiro, and M. Crespi, "Mixture of biomass to energy reuse," *Journal of Thermal Analysis and Calorimetry*, vol. 131, no. 1, pp. 765-769, 2018.
- [71]J. A. Pazo, E. Granada, A. Saavedra, P. Eguia, and J. Collazo, "Biomass thermogravimetric analysis: uncertainty determination methodology and sampling maps generation," *Int J Mol Sci*, vol. 11, no. 7, pp. 2701-14, Jul 15 2010.
- [72]D. C. S. P. LAS PROPIEDADES, "Process optimization of sampling and determining the uncertainty associated with the properties of solid fuels for cocombustión optimización del proceso de muestreo y determinación de la incertidumbre asociada a," *Dyna*, vol. 77, no. 161, pp. 109-119, 2010.
- [73]J. A. PAZÓ, E. Granada, A. Saavedra, X. Estevez, and R. Comesana, "Process optimization of sampling and determining the uncertainty associated with the properties of solid fuels for cocombustion," *Dyna*, vol. 77, no. 161, pp. 109-119, 2010.

- [74]J. A. Pazó, E. Granada, Á. Saavedra, D. Patiño, and J. Collazo, "Heterogenic solid biofuel sampling methodology and uncertainty associated with prompt analysis," *International journal of molecular sciences*, vol. 11, no. 5, pp. 2118-2133, 2010.
- [75]Z. Yildiz, H. Uzun, S. Ceylan, and Y. Topcu, "Application of artificial neural networks to co-combustion of hazelnut husk-lignite coal blends," *Bioresour Technol*, vol. 200, pp. 42-7, Jan 2016.
- [76]M. Sharara and S. Sadaka, "Thermogravimetric analysis of swine manure solids obtained from farrowing, and growing-finishing farms," *Journal of Sustainable Bioenergy Systems*, vol. 4, no. 1, p. 75, 2014.
- [77]M. V. Kok and E. Ozgur, "Characterization of lignocellulose biomass and model compounds by thermogravimetry," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 39, no. 2, pp. 134-139, 2017.
- [78]R. N. Coimbra, S. Paniagua, C. Escapa, L. F. Calvo, and M. Otero, "Combustion of primary and secondary pulp mill sludge and their respective blends with coal: A thermogravimetric assessment," *Renewable Energy*, vol. 83, pp. 1050-1058, 2015.
- [79]E. V. Canettieri, G. J. de Moraes Rocha, and J. A. de Carvalho Junior, "Investigation of characteristics of cellulign by thermogravimetric analysis."
- [80]J. Gaitán-Álvarez, R. Moya, A. Puente-Urbina, and A. Rodríguez-Zúñiga, "Thermogravimetric, Devolatilization Rate, and Differential Scanning Calorimetry Analyses of Biomass of Tropical Plantation Species of Costa Rica Torrefied at Different Temperatures and Times," *Energies*, vol. 11, no. 4, p. 696, 2018.
- [81]L. Sørum, M. Grønli, and J. Hustad, "Pyrolysis characteristics and kinetics of municipal solid wastes," *Fuel*, vol. 80, no. 9, pp. 1217-1227, 2001.