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## **Chapter 5**

# **Thermochemical Characteristics of Lignocellulosic Biomasses**

## **Abstract**

In this chapter the results of proximate, ultimate, compositional analyses and some physical properties of wheat straw (WS), rice straw (RS), banana trunk (BT), rice husk (RH), arhar stalk (AS), sugar cane bagasse (SB), sugar cane leaves (SCL), peanut shell (PS) and paper mill waste (PMW) are presented and discussed. These biomasses were selected for the study in view of their abundant availability in the most of the Indian states. These biomasses were selected for the study in view of their abundant availability in the most of the Indian states. The functional groups of each biomass have been determined using FTIR. It has been observed that alcoholic and phenolic groups, alkanes and alkenes and some aromatic molecules are present in all biomasses. Thermal degradation of all biomasses has been investigated using a TGA/DTA unit. The maximum weight loss has been recorded within the temperature range of 200–500°C in all cases. The experimental procedure and description about all equipment are already discussed in Chapter 4.

### **5.1 Biomass selection and sample preparation**

For thermo-chemical characterization experiments in all nine biomasses- arhar stalk, banana trunk, paper mill waste, peanut shell, rice husk, rice straw, sugar cane bagasse, sugar cane leaves, and wheat straw were sampled and prepared for analysis as described in Section 4.1 Chapter 4. The powdered samples thus prepared were used for thermo-chemical characterization and thermal degradation studies using a TG/DTG analysis unit as discussed below.

## 5.2 Thermo-chemical Characterization

### 5.2.1 Proximate analysis

Values of proximate analysis results are the frequently used characteristics of biomass and other solid fuels and provide information about their use as a fuel and for obtaining valuable end-products (solid, liquid and gas). Proximate analyses of all nine biomass samples were carried out in triplicate to determine moisture, volatile matter, fixed carbon, and ash contents. The average values of these parameters with standard deviation are reported in Table 5.1.

From Table 5.1, it is seen that wheat straw has the highest moisture content and arhar stalk the lowest. Moisture content is the undesirable parameter of the biomass as it uses part of the energy for evaporation rather than contributing to it (Motghare et al., 2016). Higher the moisture content lower is the heating value and consequently the reduced energy production per unit mass (García et al., 2012; Rambo et al., 2015). The moisture content also affects the quality of products of gasification and pyrolysis (Sansaniwal et al., 2017; Susastriawan et al., 2017).

The FC and VM represent the combustible matter or the stored energy in the biomass (Sanchez-Silva et al., 2012). The VM generally includes the biomass aroma, carboxylic acids, phenols, hydrocarbons, CO, CO<sub>2</sub>, H<sub>2</sub>, moisture and tars (Vassilev et al., 2010). From Table 5.1 it is seen that the VM of the biomasses has varied in the order- SB > WS > PMW > SCL > AS > PS > BT > RS and > RH. The FC has varied from 6.00 to 18.43 % (Table 5.1) and decreases in the order- PS > AS > PMW > RS > SB > BT > WS > SCL > RH. The higher the (VM/FC) ratio, higher is the available energy in the biomass. Virgin biomass is a

complex mixture of organic compounds out of which several low molecular weight compounds (such as biomass aroma, carboxylic acids, phenols, etc.) are volatile and also water soluble. High molecular weight constituents like cellulose and hemicellulose may also result into some low molecular weight water soluble compounds but most of these including lignin get charred contributing to the fixed carbon (FC). Thus volatile matter (VM) may be considered as a representative of simple water soluble compounds that will undergo microbial degradation during fermentation. Thus (VM/FC) can be considered as an indicator of bio-degradability of biomass during the initial phases of bioconversion (Disco et al., 2017; Brandt et al., 2013; Sanchez-Silva et al., 2012, McKendry et al., 2002)

Ash content represents the inorganic fraction of the biomass that remains after combustion and it varies from 1 to 40% for wood and agricultural biomasses (García et al., 2012). The ash content has been found to be the maximum in RH and minimum in AS (Table 5.1). Higher ash content results in low energy production per unit biomass and has an adverse effect on the combustion process and results in generation of large amount of ash (Motghare et al., 2016).

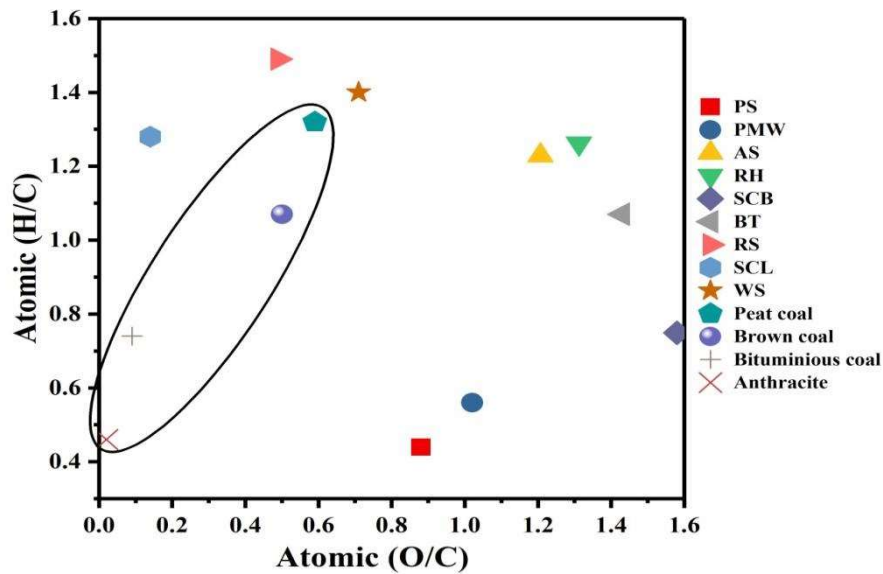
### **5.2.2 Ultimate analysis**

The ultimate analysis (elemental composition) is useful for computing the calorific value and it also indicates the fuel efficiency of the biomass. The values of C, H, O, and N contents of six biomasses studied are reported in Table 5.1. The carbon content of a biomass is directly related to its heating value (Mishra and Mohanty, 2018). The carbon contents of the studied biomasses have varied in the order SCL > PS > RS > PMW > WS > SB > AS > RH > BT. O/C and H/C ratios give an indication of the fuel quality of a

combustible material. The H/C ratios have varied from 1.02 to 1.58 and O/C from 0.13 to 1.43 (Table 5.1). Higher H/C ratio of biomass indicates ease of ignition of the fuel (Mishra and Mohanty, 2018). The molar ratio (H/C) of lignocellulosic biomasses decreases in the order SB > RS > WS > RH >SCL > AS >BT> PMW > PS. Due to the higher ratio of H/C, sugar cane bagasse is easy to burn. These ratios are also useful for preparing and comparing the van Krevelen plot for various solid fuels.

### **5.2.3 van Krevelen plot**

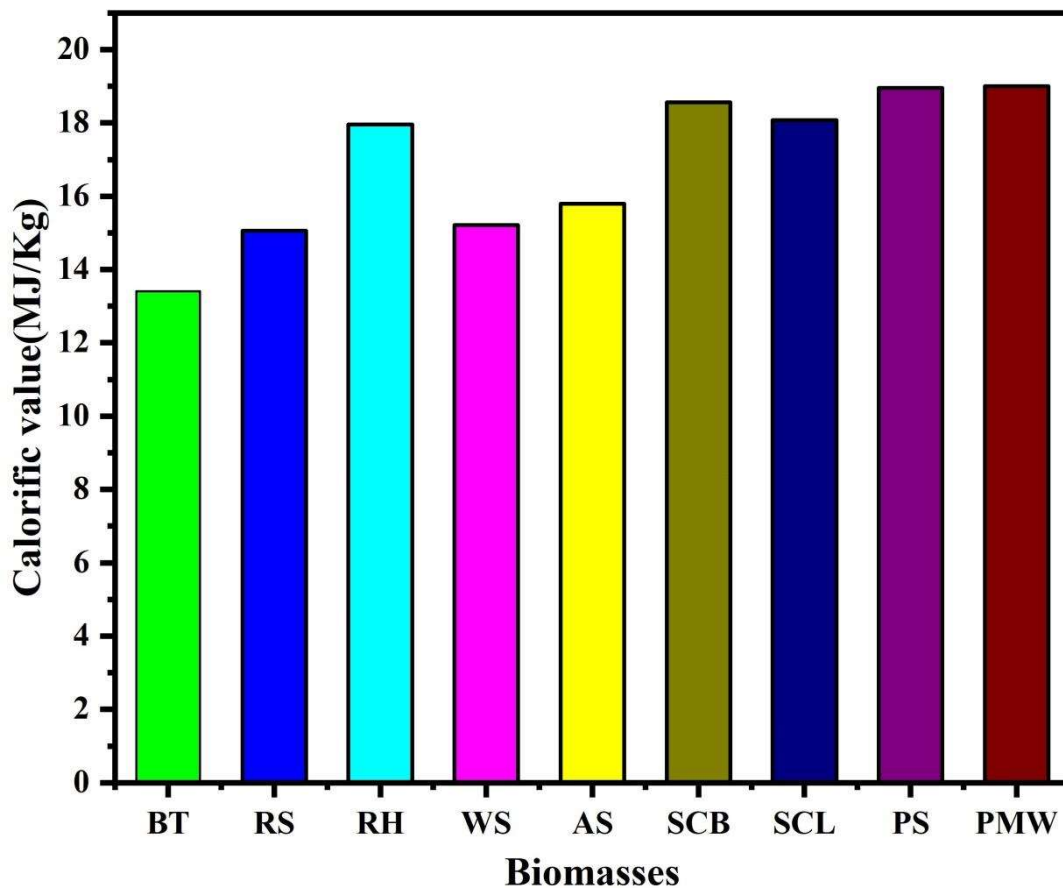
The proximate and ultimate analysis results and (H/C) and (O/C) ratios are indicative of the combustion efficiency of fuel. The van Krevelen plot (H/C versus O/C plot) is used to assess the fuel efficiency of various fuels. It is used to correlate qualitatively the compositional differences with the energy content (Chen et al., 2018). The van Krevelen plots for nine biomasses studied in this work together with that for coals (peat, brown, bituminous, and anthracite coal) (Fantini, 2017) are shown in Fig. 5.1. A higher ratio of (H/C) reflects the higher energy content and higher (O/C) reflects a lower energy content of the biomass due to the lower energy content of C-O bond compared to C-H bond. From Fig.5.1 it can be seen that the anthracite and bituminous coals have lower values of H/C and O/C and are followed by brown coal and peat. The nine biomasses included in this plot exhibit a wider variation due to the higher oxygen content in lignocellulosic compounds. It can be seen from Fig.5.1 that rice straw, wheat straw and sugar cane bagasse are close to peat and other six are far from the coals.



**Fig. 5.1** van Krevelen diagram: H: C versus O: C plot for biomasses used

#### 5.2.4 Calorific value

The calorific value (CV) is a quantitative measure of the energy content per unit mass of a fuel that could be released from a biomass through combustion. The CV for all nine biomasses used in this work is reported in Table 5.1. The paper mill waste (PMW) has the highest CV (19.00 MJ/kg) and banana trunk (BT) the lowest (13.406 MJ/kg). The calorific values of WS, RS, AS are nearly similar, with the highest for AS and the lowest for RS. The relative order of CV for nine biomasses is  $PMW > PS > SB > SCL > RH > AS > WS > RS > BT$ . It is interesting to see that the order of this variation correlates with the (H/C) ratio with the exception of RH. The variation of calorific value (HHV, MJ/kg) with types of biomasses are depicted in Fig. 5.2

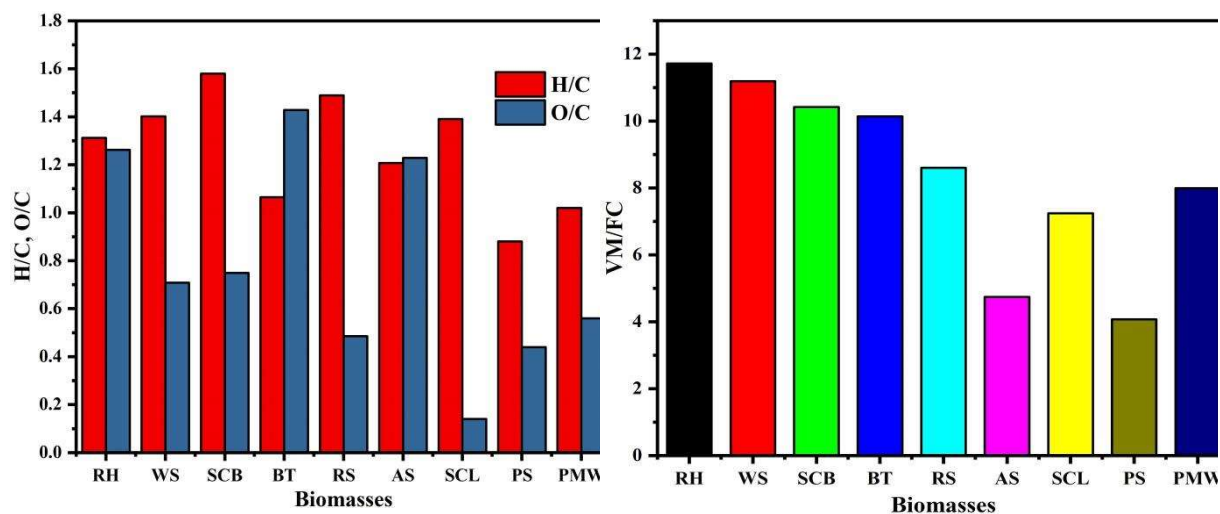


**Fig. 5.2** Variation of calorific values (HHV, MJ/kg) of various biomasses

### 5.3 Biofuel reactivity

The (H/C), (O/C), and (VM/FC) ratios determine the biofuel reactivity (Miranda et al., 2009; Green half et al., 2012; Doshi et al., 2014; Mishra and Mohanty, 2018). These ratios for all the nine biomasses investigated in this work are listed in Table 5.1 and depicted in Fig. 5.3. The level of (VM/FC) influences the fuel reactivity to a greater extent. It is seen that (H/C) and (O/C) values are nearly similar for all the nine biomasses but there is about two times variation in the (VM/FC) ratio (4.07 to 12.12). A biomass having higher (VM/FC) ratio is more reactive and a suitable candidate for the thermochemical conversion. For all biomasses studied in this work this ratio is higher than that for various

types of coal that varies from 0.09 to 2.86 (Fantini. 2017), thus indicating their high reactivity as well suitability for use as a solid fuel. Low (O/C) and high (H/C) ratios are indicative of high heating value (Mishra and Mohanty, 2018).



**Fig. 5.3** Biofuel reactivity of biomasses used

#### 5.4 Compositional analysis

The cellulose, hemicellulose and lignin contents are useful for the assessment of biomass as a potential feedstock for energy and bio-oil. The cellulose is a carbohydrate (a polymer of hexose e. g. glucose) and is the main constituent of biomass while the hemicellulose consists of short and highly branched chain polymeric molecules of pentose. The results of the compositional analysis show that PS has the highest cellulose, AS the lowest (Table 5.1). The lowest lignin content is in SB and the highest in RH. Higher the cellulosic content in the waste biomass, the higher is its biodegradation and thermal degradation rates (Mansaray and Ghaly, 1999). For example the ethanol production through fermentation is related to cellulose and hemicellulose and the resultant sugars released from the biomass feedstock through hydrolysis (Disco et al., 2017). Lignin inhibits fermentation to yield

ethanol and it has wide thermal degradation temperature range and leads to tar formation during pyrolysis, thus indicating that a biomass with high lignin content is not favorable for gasification and production of gaseous and liquid fuels through pyrolysis.

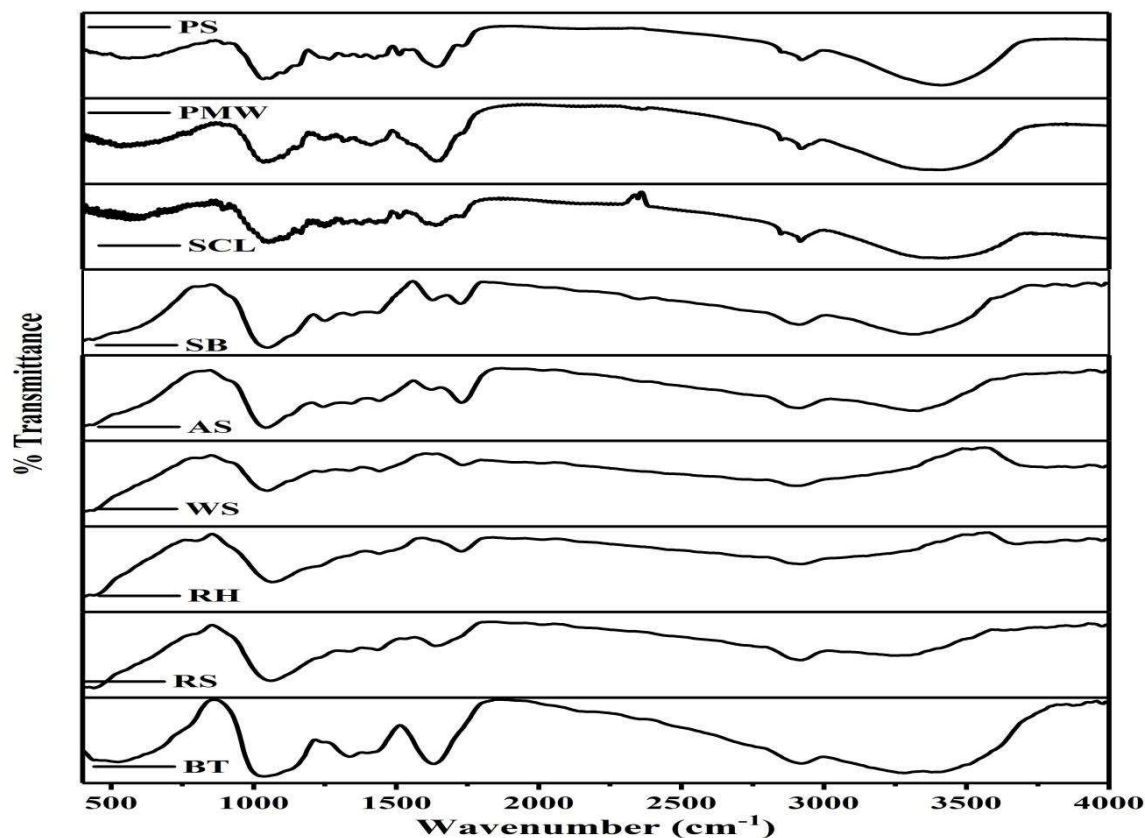
**Table 5.1:** Thermochemical properties of selected biomasses

Analysis	Rice husk (RH)	Wheat straw (WS)	Sugar cane bagasse (SB)	Banana trunk (BT)	Rice straw (RS)	Arhar stalk (AS)	Sugar cane leaves (SCL)	Peanut shell (PS)	Paper mill waste (PMW)
<b>Proximate analysis (wt %)</b>									
Moisture content	6.33 ± 0.58	7.67 ± 0.58	7.41 ± 0.57	6.67 ± 1.53	7.00 ± 0.00	4.67 ± 0.56	5.67 ± 0.36	3.40 ± 0.31	5.86 ± 0.56
Volatile matter	70.33 ± 1.15	78.33 ± 1.52	80.98 ± 0.65	74.33 ± 0.58	71.67 ± 1.15	77.33 ± 0.58	77.33 ± 0.68	75.1 ± 0.39	77.90 ± 0.68
Ash content	17.33 ± 0.58	7.00 ± 0.21	4.09 ± 0.52	11.67 ± 1.15	13.00 ± 1.00	1.67 ± 0.58	10.67 ± 0.41	3.07 ± 0.26	6.50 ± 0.41
Fixed carbon	6.00 ± 1.00	7.00 ± 2.20	7.52 ± 0.25	7.33 ± 0.25	8.33 ± 2.08	16.33 ± 1.15	6.38 ± 1.02	18.43 ± 0.32	9.74 ± 1.02
VM/FC ratio	11.72 ± 1.15	11.19 ± 0.69	10.77 ± 2.6	10.14 ± 2.32	8.60 ± 1.15	04.74 ± 0.50	12.12 ± 0.17	4.07 ± 0.31	7.99 ± 0.17
<b>Ultimate analysis (wt %)</b>									
Carbon	35.58	48.24	46.19	33.09	55.79	36.19	76.83	58.71	53.75
Hydrogen	3.88	5.64	6.11	2.94	6.93	3.64	8.19	4.32	4.57
Oxygen	59.79	45.55	47.11	63.03	36.12	59.35	14.39	34.25	40.67
Nitrogen	0.80	0.56	0.59	0.94	1.16	0.42	0.59	2.72	1.01
<b>Sulphur</b>	-	-	-	-	-	-	-	-	-
O/C ratio	1.26	0.71	0.75	1.43	0.49	1.23	0.13	0.88	0.56
H/C ratio	1.31	1.40	1.58	1.07	1.49	1.21	1.27	0.44	1.02

Calorific value (MJ/kg)	17.96	15.29	18.56	13.41	15.06	15.80	18.08	18.95	19.00
<b>Compositional analysis (wt %)</b>									
Hemicellulose	19 ± 0.39	36 ± 0.65	26 ± 0.32	25 ± 0.61	26 ± 0.56	18 ± 0.53	42 ± 0.46	18.70 ± 0.23	
Cellulose	32 ± 0.21	35 ± 0.29	43 ± 0.19	25 ± 0.49	40 ± 0.27	24 ± 0.57	44 ± 0.51	43.45 ± 0.26	
Lignin	26 ± 0.31	18 ± 0.38	12 ± 0.36	15 ± 0.42	19 ± 0.26	19 ± 0.37	17 ± 0.39	19.55 ± 0.42	

## 5.5 FTIR spectroscopic analysis

The FTIR spectroscopic analysis was conducted to know the chemical functional groups present in various biomasses. It is also used to identify the presence of main biomass constituents (hemicellulose, cellulose and lignin), which are responsible for change in the thermochemical conversion behavior (Fig. 5.4). The FTIR spectral peaks in the range of  $3600\text{-}3400\text{cm}^{-1}$  reflect the presence of alcoholic phenols, aromatics, protein, and water and are attributed to the axial deformation of O-H and -N-H groups. All the biomasses showed peaks between  $3400\text{-}3200\text{cm}^{-1}$  representing the O-H stretching of phenol and alcohols due to stretching of O-H groups present in cellulose and lignin chains (Biswas et al., 2017). Peaks around  $2918\text{cm}^{-1}$  indicate asymmetric and symmetric methyl group stretching's. Presence of C-H group vibrations of alkane lies in the range of  $3000\text{-}2800\text{cm}^{-1}$ . The bands at about  $1733\text{cm}^{-1}$  and  $1243\text{cm}^{-1}$  are due to C=O and C-O bonds in hemicellulose (Yuan et al., 2015). Spectral bands between  $1725\text{-}1715\text{cm}^{-1}$  represent the C=O stretch of the ester, ketone and carbonyl groups. Peaks between  $1616\text{-}1648\text{cm}^{-1}$  represent the C=C stretch of alkenes. Peaks corresponding to ( $1640\text{-}1616\text{cm}^{-1}$ ) indicate the aromatic C = C ring that indicate the presence of lignin and protein in the biomass (Mishra and Mohanty, 2018). Peaks around  $1340$  to  $1500\text{cm}^{-1}$  are associated with alkenes,  $\text{CH}_2$ ,  $\text{CH}_3$  and confirm the presence of cellulose and hemicellulose. Bands between  $1230\text{-}1030\text{cm}^{-1}$  represents C-N stretching of the amine group. Spectral peaks around  $1059\text{cm}^{-1}$  indicate deformation of (C-O symmetric stretching of carbohydrate and alcoholic molecule indicating presence of polysaccharides) and indicate presence of cellulose and hemicellulose. Peaks between  $450\text{-}900\text{cm}^{-1}$  indicate presence of aromatic groups (Mothé and De Miranda, 2009; Naik et al., 2010; Quan et al., 2016; Mishra and Mohanty, 2018)

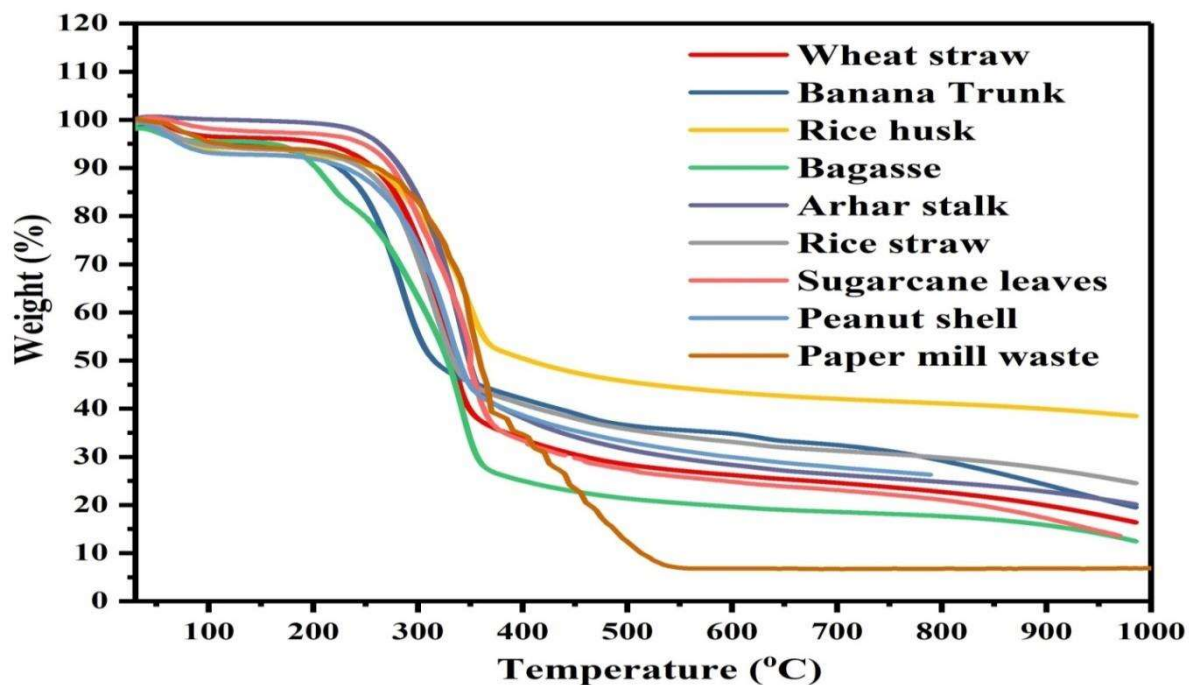


**Fig 5.4** FTIR spectra of all selected nine biomasses

## 5.6 TG and DTG analyses results

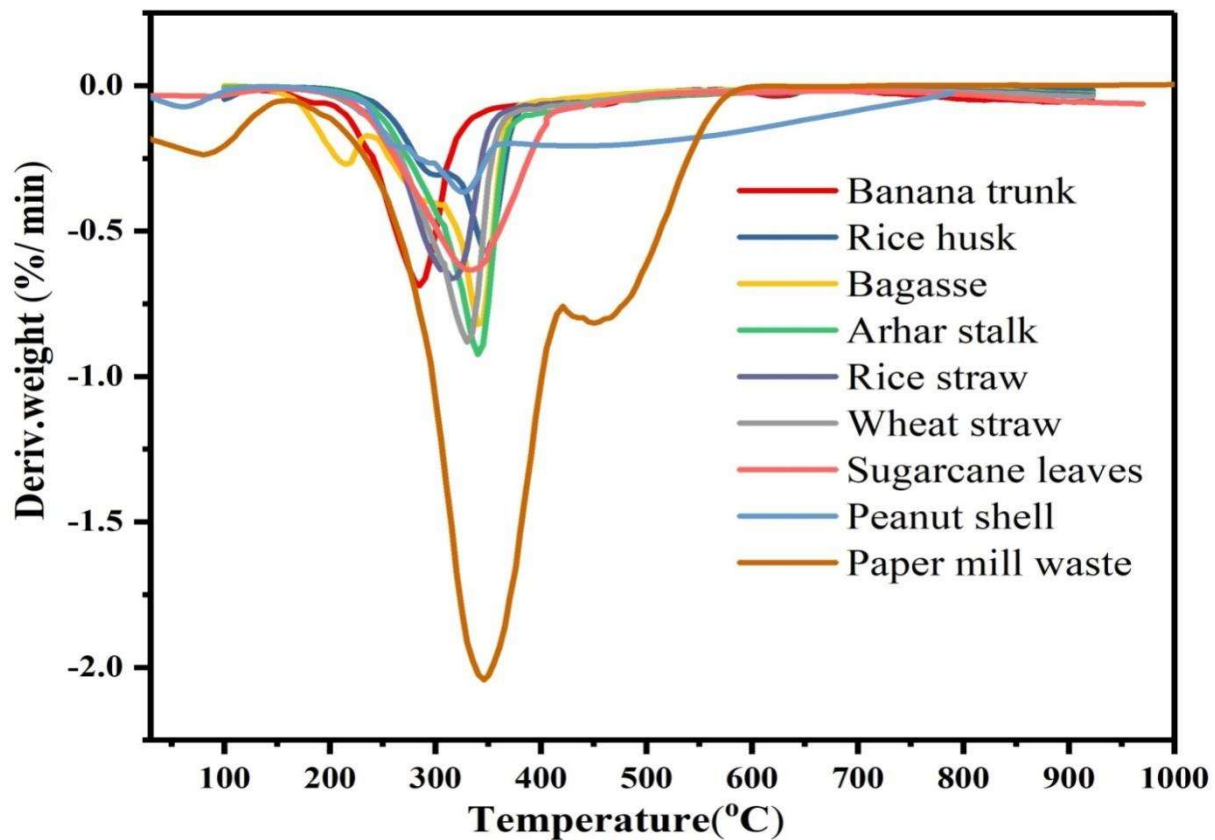
The thermal decomposition profiles of all nine biomass samples at a heating rate of 10°C/min with a N<sub>2</sub> flow rate of 20ml/min are depicted in Fig. 5.5. The comparative degradation profiles of samples with temperature which varied from ambient (30°C) to 1000°C for all nine biomasses are shown in this figure. Values of initial and final degradation temperatures, weight loss (%), degradation rate (%/°C), and residual weight (%) derived from TGA and DTG analyses are listed in Table 5.2. The analysis of thermal degradation rate helps in assessing the potential of a biomass feedstock for energy production and gives an idea about variation in the thermal decomposition process with

increase in temperature (Mansaray and Ghaly, 1999). From the profile of the thermal decomposition behavior of nine biomasses used, it is seen that the TGA curves are divided into four stages: i) below 200°C release of the initial moisture content of sample or drying takes place together with release of some volatile components and after that major components start decomposing, some hemicellulose may also degrade in this stage, ii) hemicellulose and cellulose decomposition occurs in the temperature range of 200 to 350°C, iii) cellulose degradation continues in the range of 350 to 500°C, and iv) lignin is not easy to decompose as it contains aromatic rings, various side chains, and chemical bonds which resist thermal degradation and most of it gets degraded in the temperature range of 500 to 1000°C (Biswas et al., 2017; Plis et al., 2016; Quan et al., 2016). The total solid residue of each biomass (char) left after complete decomposition is given in Table 5.2.



**Fig. 5.5** The TGA curves of biomasses used

The derivative thermogravimetric (DTG) temperature plots for all nine biomass samples are shown in Fig. 5.6. Mainly two peaks that depend on the cellulose and hemicellulose contents of the biomass are observed in each case. The first peak is in the range 200- 280°C while the second peak is in the range 280- 480°C. The major constituents of lignocellulosic biomasses decompose thermo-chemically within this temperature range. Maximum hemicellulose and cellulose degradation occurs in the temperature range of 200- 350°C and degradation of some cellulose continues up to 500°C. Lignin degrades beyond 500°C and continues up to 1000°C (Kumar et al., 2019; Mansaray et al., 1998).



**Fig 5.6** The DTG curves of various biomasses used

**Table 5.2:** Thermo-gravimetric and differential thermogravimetric analyses parameters analyses.

Biomass	Initial degradation temperature (T <sub>i</sub> <sup>o</sup> C)	Final degradation temperature (T <sub>f</sub> <sup>o</sup> C)	Weight loss (%)	Average degradation rate (%/°C)	Residual weight (%) at the end of stage IV
<b>Stage I</b>					
Banana trunk	29.94	200	7.47	0.0309	
Sugarcane bagasse	30.59	200	8.94	0.0548	
Rice husk	30.11	200	7.51	0.0135	
Arhar stalk	30.21	200	0.69	0.0081	
Rice straw	29.88	200	6.66	0.0137	
Wheat straw	29.98	200	4.49	0.0122	
Sugarcane leaves	30.20	200	2.92	0.0500	
Peanut shell	30.26	200	9.21	1.4000	
Paper mill waste	30.45	200	8.24	0.0500	
<b>Stage II</b>					
Banana trunk	200	350	50.66	0.3046	
Sugarcane bagasse	200	350	63.03	0.3822	
Rice husk	200	350	34.04	0.2147	
Arhar stalk	200	350	50.75	0.3405	
Rice straw	200	350	51.53	0.3225	
Wheat straw	200	350	58.53	0.3727	
Sugarcane leaves	200	350	61.25	10.250	
Peanut shell	200	350	49.34	5.2300	
Paper mill waste	200	350	60.28	2.0000	

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**Stage III**

Banana trunk	350	500	19.70	0.0597
Sugarcane bagasse	350	500	36.32	0.0914
Rice husk	350	500	25.16	0.1088
Arhar stalk	350	500	35.54	0.1265
Rice straw	350	500	20.93	0.0645
Wheat straw	350	500	28.26	0.0792
Sugarcane leaves	350	500	25.23	5.1200
Peanut shell	350	500	10.23	7.9400
Paper mill waste	350	500	35.23	0.5750

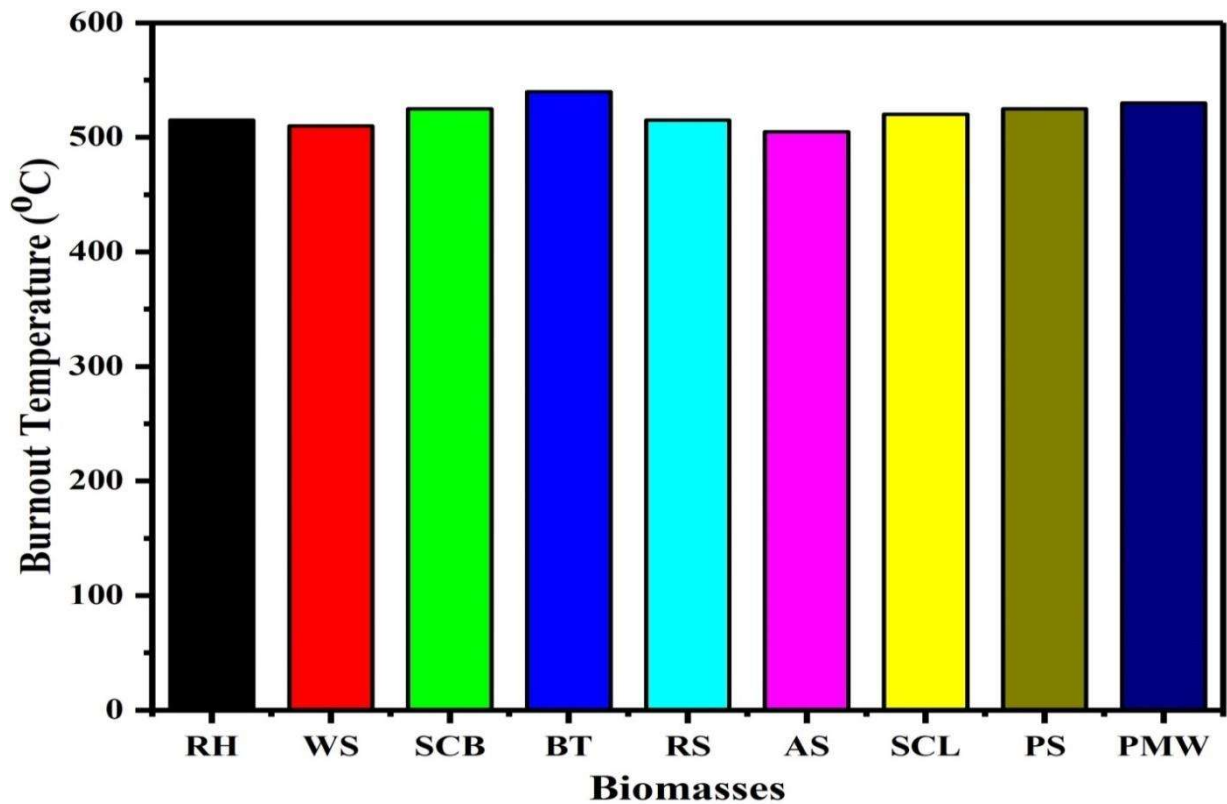
**Stage IV**

Banana trunk	500	1000	37.35	0.032	19.48
Sugarcane bagasse	500	1000	29.18	0.015	12.46
Rice husk	500	1000	13.19	0.014	38.46
Arhar stalk	500	1000	29.74	0.022	20.11
Rice straw	500	1000	24.89	0.021	24.51
Wheat straw	500	1000	32.83	0.022	16.38
Sugarcane leaves	500	1000	12.32	0.050	12.23
Peanut shell	500	1000	5.120	0.400	25.23
Paper mill waste	500	1000	3.232	0.050	5.230

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## 5.7 Burnout temperature

The burnout temperature is an important characteristic parameter of solid carbonaceous fuels and is used for evaluating the pyrolysis and combustion behaviour (El-Sayed and Mustafa, 2014; Moghtaderi, 2007; Mishra and Mohanty, 2018). It is the temperature at which rate of degradation homologically decreases to less than 1% per degree C. It was investigated for all the nine biomasses at the heating rate of 10°C/min. The lowest burnout temperature was obtained for arhar stalk (505 °C) and the highest for banana trunk (540°C). The decreasing order of burnout temperature is as: BT > SB >PMW >RH >PS > SCL >RS > WS > AS. Variation of the burnout temperature is due to the variation in the composition of biomasses (Fig. 5.7).



**Fig. 5.7** Burnout temperature of biomasses used

## **5.8 Conclusion**

The thermogravimetric analyses of nine biomasses studied in this work showed more or less similar TGA curve profiles, but exhibited difference in the degradation temperature range and residual mass values. Degradation profile of all nine biomasses showed that the maximum weight loss was observed between temperature range 200-500 °C. The results demonstrate that each type of biomass has a specific degradation rate which depends on its cellulose, hemicellulose, and lignin contents.

On the basis of various thermochemical characteristics such as volatile matter, calorific values, cellulose content, abundant availability, less suitability as fodder for animals, it is possible to select biomasses for gasification and pyrolysis on large scale. Therefore, sugarcane leaves (SCL), peanut shell (PS), banana trunk (BT) and paper mill waste (PMW) were selected for further in details kinetic analysis of pyrolysis using TGA and pyrolysis product yield using lab scale fixed bed reactor.