Chapter 3

Torrefaction of woody biomass (*Acacia nilotica*): Investigation of fuel and flow properties to study its suitability as a good quality solid fuel

General background

This chapter aimed to investigate the torrefaction of *Acacia nilotica* in a quartz tube fixed-bed reactor to examine the suitability of torrefied *Acacia nilotica* as a good quality solid fuel. Temperature and retention time varied from 220-280 ℃ and 20-60 min, while, heating rate was kept constant at 15 ℃/min. The fuel (volatile ignitability (VI), combustibility index (CI), fuel ratio (FR)), and flow (Hausner ratio (HR), cohesion coefficient (C), Carr compressibility index (CCI), angle of repose,) properties were investigated for raw and torrefied biomass. Torrefied *Acacia nilotica* was also characterized through TGA, FTIR, SEM-EDX and ICP-MS analysis. For moisture sorption test, contact angle was measured. Finally, torrefied *Acacia nilotica* was compared with coal using published literature.

3.1 Introduction

Over the last few decades, the rapid increase in world population, industrialization and high living standard of people, created a huge gap between demand and supply of energy (Song et al., 2018). To fulfill the energy demand, only coal contributes 38 % of total electricity generation of the world in 2017 (Magalhães et al., 2019). The reserves of fossil fuel such as coal, petroleum, and natural gas are limited and large exploitation along with complete dependency on the fossil fuel can diminish the fossil fuel reserve. Also, application of fossil fuels severely affects the environment by harmful emission such as SO_x, NO_x, greenhouse gas (CO_2) and particulate matters (Yue et al., 2017). The most promising way to solve the problem is to use and extract energy from renewable resources (Yang et al., 2019).

Though we have wind, solar, geothermal, hydrothermal etc. as renewable energy sources, however, among them biomass is most abundant worldwide and easily available. The consideration of biomass as a carbon-neutral fuel and its quality to emit lesser amount of sulfur and nitrogen makes it important source for the production of bio-energy (Giudicianni et al., 2013). *Acacia nilotica*, a kind of forest tree, has vast availability in India, Australia, African, and South East Asian countries (Bargali & Bargali, 2009). It is a tropical tree having height around 7 to 18 m and diameter around 20 to 30 cm (Raj et al., 2015). These trees are fast growing, generally found in waste and barren land having low productivity and it does not compete with land application for food production. It is also considered as an important plant having economic value since it is a medicinal plant and good source of tannins and gums (Bargali & Bargali, 2009; Saratale et al., 2019). In addition, it is a good source of timber wood and used as a fuel and fodder for animals in rural areas in India.

Acacia nilotica is dispersed all over India along national highways, railway lines, forest areas, roadsides, farmlands, tank foreshores, farm fields, village grazing lands and wastelands. The total wood production from *Acacia nilotica* is 167 tonnes per hectare, while, total pod generation from *Acacia nilotica* is 0.6 million tonnes per year (Pandey & Sharma, 2005; Singh et al., 2019b; Singh et al., 2020b). As a fuelwood it is considered as an excellent material as it has high calorific value (~20 MJ/kg) and lesser smoke emission tendency (Pandey & Sharma, 2005). It is also used in pulp and paper industry and as a fuel in textile and brick kiln (Singh et al., 2020b). Also, the charcoal made from *Acacia nilotica* has superior properties from the other biomass species. Different part of *Acacia nilotica* tree (leaf, seed and bark) are used as adsorbent and feedstock for pyrolysis process (Garg et al., 2016; Gupta & Lataye, 2019).

Regardless of large availability and easy accessibility, biomass is allied with many inherent disadvantages as discussed in Chapter 1. Due to these drawbacks, at present, the global annual energy achieved from biomass is approximately 10% of the overall energy consumption (Chen & Kuo, 2010; van der Stelt et al., 2011). It is therefore essential to improve the quality of biomass through pretreatment process and check the suitability of treated biomass in term of fuel and flow properties, before it can be used in thermochemical conversion process efficiently. Flow characteristics of biomass play an important role when it comes to blending biomass with other biomass, plastic materials during co-pyrolysis, and coal in co-firing process in thermal power plants. However, application of biomass in co-pyrolysis, combustion and co-firing is difficult to attain due difference in fuel and flow behavior of coal and biomass. In the past, various pretreatment methods have been explored to improve the quality of biomass. Among the various processes, torrefaction provides a promising route for the upgradation of biomass.

Torrefaction is defined as a mild pyrolysis process with the temperature zone of 200-300 ℃ at atmospheric pressure with inert medium at a low heating rate of (< 20 ℃/min) and retention time around 15-60 min (Keivani et al., 2018; Kutlu & Kocar, 2018; Manouchehrinejad et al., 2018). Many literatures are available that discuss the properties of torrefied biomass as good quality solid biofuel as discussed in Chapter 2. However, focus given on the study of fuel properties such as volatile ignitability (VI), combustibility index (CI), fuel ratio (FR) and flow properties such as Hausner ratio (HR), cohesion coefficient (C), Carr compressibility index (CCI) and angle of repose for raw and torrefied biomass and variation of these properties with process parameter during torrefaction is very less. To check the suitability of torrefied biomass as better quality solid biofuel or as a blend with coal, various tests have been performed. The fuel (volatile ignitability (VI), combustibility index (CI), fuel ratio (FR)), and flow (Hausner ratio (HR), cohesion coefficient (C), Carr compressibility index (CCI), angle of repose,) properties, particle size, density, moisture sorption (open environment test and contact angle test) of torrefied biomass were analyzed. Also, the characteristics of torrefied biomass at different conditions were analyzed through TGA, FTIR, SEM-EDX and ICP-MS analysis. Finally, the characteristics of torrefied biomass were compared with properties of coal using published literature.

3.2 Experimental section

3.2.1 Materials

The wooden block of *Acacia nilotica*, about 1 ft in diameter was collected from village close to Banaras Hindu University (BHU) campus, Uttar Pradesh, India. The collected biomass was chopped into smaller with the help of an axe and further, fine particles between 0.7 to 1.25 mm were obtained after subsequent cutting (Cutting machine; Retsch model SM 300, Germany) and screening. The surface moisture of the biomass was removed by sun drying. After that biomass sample was again kept in an oven kept at 80 ℃ for overnight and then kept in air tight container prior to experiments. In the present work, dried *Acacia nilotica* is labeled as DAN and torrefied *Acacia nilotica* is labeled as TAN-X-Y-Z, where X indicates the torrefaction temperature, Y indicates the retention time and Z indicates the heating rate. For example, TAN-250-60-15 indicates torrefied *Acacia nilotica* which was obtained by torrefaction at 250 ℃, 60 min retention time and 15 ℃/min heating rate.

3.2.2 Experimental setup and procedure for torrefaction

The schematic diagram of the experimental setup is shown in Fig. 3.1. It consists of temperature controller unit and a fixed-bed reactor (Inner diameter = 2.5 cm, length = 80 cm) made up of quartz, split tube furnace (NSW-104 New Delhi), recirculating bath (Eyela CA-1112CE, Japan), and a counter-current condenser unit. In each experiment, 10 g of biomass sample was loaded into the reactor on a support of ceramic wool. The height of sample in the reactor was around 10 cm. A K- type thermocouple was inserted into the reactor for measuring the temperature of torrefaction. The tip of the thermocouple just touched the upper surface of sample. The reactor was then purged by nitrogen gas (99.999% purity, Ashish Enterprise, Varanasi) at a flow rate of 45 mL/min using mass flow controller (Bronkhorst, Netherlands) for 30 min to remove oxygen trapped into the bed. Then, the furnace was turned on and heating rate was measured from control panel of furnace. The torrefaction of biomass was carried out between 220-280 ℃ with retention time between 20-60 min at a heating rate of 15 ℃/min. In each case, when the retention time was over the furnace automatically started cooling. The solid residue (torrefied biomass) was taken out of the reactor when room temperature reached. All the experiments were performed twice and average values were reported.

The solid yield of biomass is calculated as:

$$\textit{Solid yield (SY)} = \frac{m_{TAN}}{m_{DAN}} \tag{3.1}$$

where m_{TAN} is the mass of torrefied *Acacia nilotica* at different process parameter and m_{DAN} is the mass of dried *Acacia nilotica*.

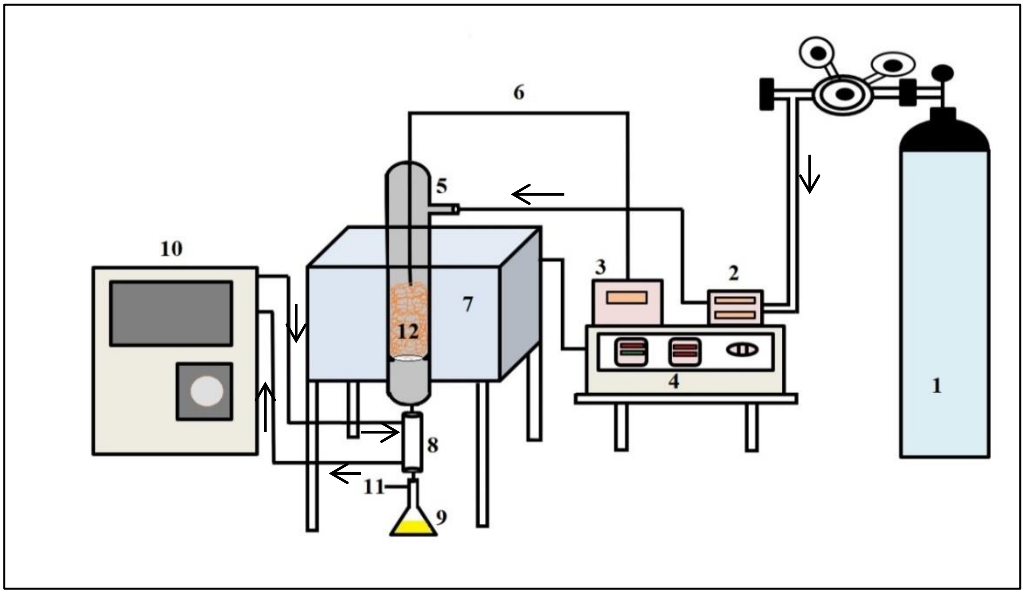

Figure 3.1 Schematic diagram of experimental set-up: 1-nitrogen cylinder, 2-mass flow controller, 3-temperature measuring unit, 4- split tube furnace (NSW-104) controller, 5-long tube fixed bed reactor, 6-K-type thermocouple, 7- split tube furnace (NSW-104), 8-condenser, 9-oil collector, 10- chiller (Eyela CA-1112CE), 11-gas collector, 12-biomass with ceramic wool bed (Singh et al., 2020b).

Table 3.1 List of controlled and measured variable during experiment

Variable	**Range/value**
Controlled variable	
Heating rate (°C/min)	15
Sweeping gas flow rate (mL/min)	40
Particle size (mm)	0.7-1.25
Pressure	Atmospheric
Measured variable	
Temperature (°C)	220-280
Retention time (min)	20-60

Table 3.2 Specifications/detail of instruments/variables used in experimental setup and procedure

Variable/analysis	Instrument name/specification	Measurement Range	Uncertainty (%)
Temperature (℃)	K-type thermocouple	-270 to 1370 ℃	±1.1 ℃
Split tube furnace (NSW-104)	Single heating zone (length 455 mm)	Max. 900 ℃	
	Micro processing PID controller		
	Work on 220 volt AC 50 Hz		
Heating rate (℃/min)	Set from control panel of furnace	-	±0.15 ℃/min
Retention time (min)	Set from control panel of furnace	-	Nil
Nitrogen flow rate (mL/min)	Mass flow controller (Bronkhorst)	0 to 200 mL/min	±0.30 % mL/min
Weighing machine	Sartorius weighing machine (BSA224S-CW)	Max. 250 g	±0.1 mg
Initial drying of sample	Laboratory Universal Hot air oven	Max. 260 ℃	±5 ℃
Proximate analysis	Muffle furnace	Max. 900 ℃	±5 ℃
Recirculating bath	Eyela CA-1112CE	-20 to 30 ℃	±2 ℃
Cutting machine	Retsch model SM 300	-	-

3.2.3 Physicochemical properties of raw and torrefied biomass

3.2.3.1 Proximate and ultimate analyses

Proximate analysis of biomass can be used to calculate moisture, volatile matter, fixed carbon, and ash content of the biomass sample. All these parameters were expressed on wet basis and dry basis and calculated using different ASTM standards mentioned in Table 3.3. The aim of ultimate analysis was to calculate the elemental composition (CHNS) of DAN and TAN. The Element analyzer (EURO EA3000, EURO VECTOR instrument and software, ITALY) was used to execute ultimate analysis. Oxygen bomb calorimeter (Rajdhani Scientific, NSTTS Co., New Delhi, India) was employed to evaluate the heating value of DAN and TAN.

The energy density ratio and energy yield can be calculated using Eqs. (3.2) and (3.3):

$$\textit{Energy density ratio (EDR)} = \frac{HHV_{db,TAN}}{HHV_{db,DAN}} \tag{3.2}$$

$$\textit{Energy yield (EY)} = SY \times EDR \tag{3.3}$$

The CHO index derived from the ultimate analysis of biomass to explain the oxidation state of carbon present in organic matter as recommended by Mann et al. (Mann et al., 2015). It can be calculated as:

$$\textit{CHO index} = \frac{2[O]-[H]}{[C]} \tag{3.4}$$

where [O], [H] and [C] are the mole fraction of oxygen, hydrogen, and carbon present in the organic material respectively.

Table 3.3 Different ASTM standards used to calculate engineering properties of torrefied biomass

Physical parameter	ASTM standard used
Bulk density	ASTM E873-82
Moisture content	ASTM E871
Ash content	ASTM E1755
Volatile matter	ASTM E872
Heating value	ASTM D240
Angle of repose	ASTM C144

3.2.3.2 Density, porosity, and particle size of raw and torrefied biomass

The density of biomass can be of three types: the bulk density, the tapped density, and the particle density. ASTM standard E873-82 is used to calculate the bulk density of biomass. The standard includes pouring the biomass sample into a standard-size container. In this study, a measuring cylinder of 500 ml is filled with biomass gently. The excess material over the cylinder was removed by a scale to level the biomass at the top of the measuring cylinder. The mass of the biomass present in the cylinder was weighed, and bulk density was calculated using the Eqs. (3.5). The tapped bulk density of biomass can be calculated by tapping the cylinder containing the biomass until it reaches a constant volume (tap around 100 times). The tapped density (ρ_{Tb}) was calculated using Eqs. (3.6). For calculation of particle density of biomass, it can be given a particular geometrical shape like cube, cuboid, sphere, and cylinder, etc. The mass of the shape and volume can be calculated, and division of both gives the particle density of biomass. The porosity of biomass sample can be defined as the pore spaces present in the bulk samples of biomass, and it can be calculated using the following Eqs. (3.8).

Bulk density, ρ_b (kg/m^3) = $\frac{m_g - m_c}{V_L}$ (3.5)

Tapped density, ρ_{Tb} (kg/m^3) = $\frac{m_t - m_c}{V_L}$ (3.6)

Particle density, ρ_p (kg/m^3) = $\frac{m_p}{V_p}$ (3.7)

$$\varepsilon_0 = 1 - \frac{\rho_b}{\rho_p} \quad (3.8)$$

where ρ_b is the bulk density, ρ_{Tb} is the tapped density, ρ_p is the density of particle, m_g is the total mass of cylinder and biomass (kg), m_c is the mass of empty cylinder (kg), m_t is the total mass of cylinder and biomass after tapping (kg), m_p is the mass of geometrical shape (kg) and V_p is the volume of geometrical shape (m^3), V_L is the volume of measuring cylinder (m^3) and ε_0 is the porosity of biomass.

However, the biomass particle having irregular shape, the volume of particle can be calculated by deploying Eqs. (3.9) given by Tooyserkani et al.(Tooyserkani et al., 2013)**.**

$$V_p = V_c - V_R\left(\frac{P_1}{P_2} - 1\right) \quad (3.9)$$

where Vp is the volume of biomass (m^3), V_C is the sample cell volume (m^3), V_R is the reference volume (m^3), P_1 is the pressure after pressurizing the reference volume (Pa), and P_2 is the pressure after including V_C (Pa).

For particle size distribution, unsieved DAN obtained after grinding was torrefied at 220, 250, and 280 ℃; then DAN and TAN was sieved and analyzed. Both, DAN and TAN were passed through a series of sieves having opening sizes (22, 25, 30, 36, 44, 52, 60 and 85 BSS) using a screen shaker. The sieves are arranged in the stack with largest opening at the top and smallest opening at the bottom. Size distribution for DAN and TAN was analyzed by employing the procedure given by American National Standards Institute (ANSI). After completion of shaking process, biomass sample accumulated on every single screen has been weighed. Geometric mean diameter (d_{gm}) for DAN and TAN was determined by employing the co-relation given by Cai et al. (Cai et al., 2017) in Eqs. (3.10).

$$d_{gm} = log^{-1}\left(\frac{\sum M_{i}.log\sqrt{d_i.d_{i-1}}}{\sum M_i}\right) \qquad (3.10)$$

where d_i is diagonal of screen apertures of i^{th} screen, d_{i-1} is diagonal of the screen apertures in the next larger screen, and M_i is the mass retained on the i^{th} screen.

3.2.3.3 Moisture sorption test of raw and torrefied biomass

3.2.3.3.1 Open environment test

In this work, the characteristics of DAN and TAN for moisture sorption were performed in an open environment (relative humidity 60 %). For calculation of amount of moisture absorbed with respect to time, the sample DAN, TAN220-40, TAN250-40, and TAN280-40 were analyzed for the purpose. Weighed samples were kept for five days in an open environment. After estimated time, the samples were taken and weighed and percentage moisture absorbed was calculated using Eqs. (3.11):

$$\% \text{ moisture absorbed} = \frac{M_{Bi} - M_A}{M_A} \times 100 \qquad i = 1 \text{ to } 5 \text{ days} \tag{3.11}$$

where M_A is the initial mass of the sample (kg), and M_{Bi} is the mass of sample after i^{th} day (kg).

3.2.3.3.2 Contact angle measurement

To check the water absorption characteristics, water contact angle of DAN and TAN were measured using contact angle analyzer (KRUSS, DSA25 Series, Hamburg, Germany). De-ionized water was used as a probe liquid. For contact angle measurement pellets from DAN and TAN were made and contact angle was recorded using a sessile drop method at room temperature.

3.2.3.4 Flowability and combustion indices of raw and torrefied biomass

The flow characteristics of DAN and TAN was investigated using Hausner ratio (HR), cohesion coefficient (C), Carr compressibility index (CCI) and angle of repose, while, fuel characteristics of DAN and TAN was investigated by fuel ratio (FR), combustibility index (CI), and volatile ignitability (VI). The detail about flow and fuel characteristics has been discussed in Chapter 1.

3.2.3.5 Analytical instruments used to characterize raw and torrefied biomass

Thermogravimetric analyzer (Perkin Elmer STA 6000) was used to investigate the thermal behavior and mass loss characteristics. 5 mg of DAN and TAN was heated from 25 to 800 ℃ in the presence of nitrogen atmosphere, at a flow rate of 20 mL/min and a constant heating rate of 5 ℃/min. Fourier Transform Infrared Spectroscopy (FTIR) was done using (FTIR, Varian 1000, USA) for qualitative analysis of functional group present in DAN and TAN after torrefaction. Oven dried Potassium Bromide (KBr) was used to make the pellets to reduce the interference from water. The spectra were recorded from 4000 to 400 cm^{-1} wavenumber. The surface morphology and elemental analysis of DAN and TAN220-40, TAN250-40, and TAN280-40) were studied by scanning electron microscopy (SEM, model JEOL JSM5410, Japan). Metal content present in DAN and TAN was determined by using inductively coupled plasma-mass spectrometer (ICP-MS Perkin Elmer Optima 7000 DV series). Sample were digested in nitric acid and diluted with double distilled water so that metal concentration falls into the detection limit.

3.3 Results and discussion

3.3.1 Solid product and energy yield of torrefied biomass

The outcomes of torrefaction process are torrefied *Acacia nilotica* as solid product, condensable liquid and gaseous products. The amount of each product varies with operating conditions such as process temperature and retention time of biomass inside the reactor. Fig. 3.2 shows the variation of solid yield with temperature and retention time during torrefaction. When process temperature during torrefaction increases, the significant cleavage of hydroxyl group associated with biomass takes place. As a result, the amount of condensable liquid product with more water vapour increases with process temperature at fixed retention time. As an example, the solid yield was 61.82% and 43.03%, when the biomass was torrefied at 220 and 280 ℃, respectively, at a constant retention time of 40 min. Hence, effectively, the solid yield decreased by 30.40% due to increase of process temperature at constant retention time. Moreover, solid yield also decreased with increase in retention time (Strandberg et al., 2015). The solid yield decreased from 60.10% to 51.23%, when the retention time was increased from 20 to 60 min, at torrefaction temperature of 250 ℃. It was observed that temperature had more pronounced effect than the retention time on torrefaction process. Subsequently, fuel and flow characteristics of torrefied *Acacia nilotica* should also be more process temperature reliant than retention time. Keeping this in mind, all the properties of torrefied *Acacia nilotica* at three temperature (220, 250, and 280 ℃) at 40 min retention time are calculated. The solid product yield from torrefaction often varies with biomass and its constituents. The biomass with higher fraction hemicellulose produces less solid product, as hemicellulose decomposition occurs at comparatively lower temperatures than cellulose and lignin (Bach & Skreiberg, 2016; Granados et al., 2016). The energy yield which is a product of solid yield and ratio of HHV of TAN to DAN indicates the amount of energy preserved in biomass after torrefaction. The energy yield of TAN220-40, TAN250-40, and TAN280-40 is found to be 74.10, 62.99, and 45.36 %, respectively. It shows that with increase in temperature the energy yield decreases since at higher temperature, dehydrogenation and deoxygenation of biomass become more prominent.

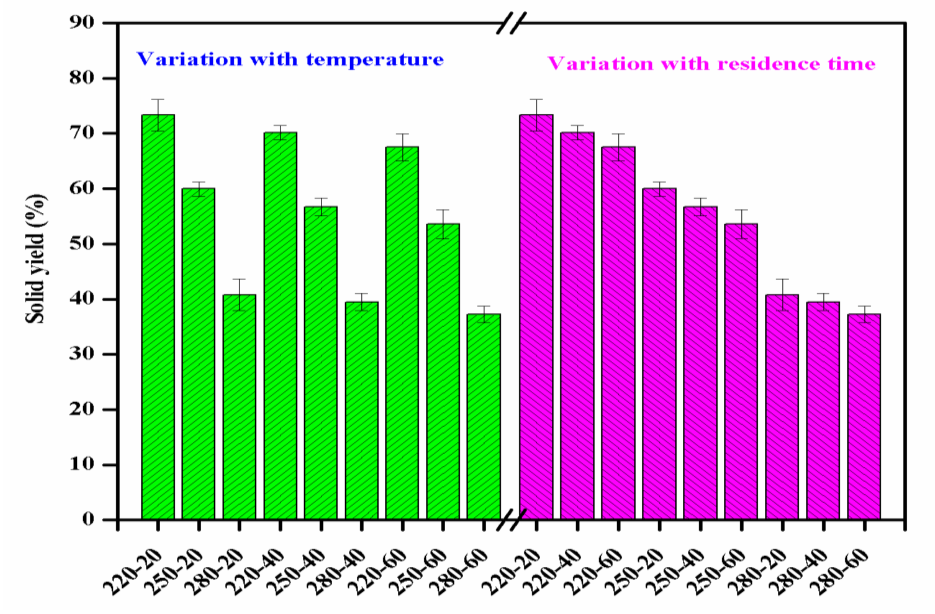

Figure 3.2 Variation of solid yield with temperature and retention time

The choice of optimum parameter for upgradation of DAN through torrefaction is based on the balance between higher heating value and energy yield of TAN. In this study, torrefaction at 250 ℃, and retention time 40 is recommended since the energy yield of TAN is 62.99 % and higher heating value is 22.54 MJ/kg.

3.3.2 Physicochemical Characteristic of raw and torrefied products

The results from physicochemical analysis are presented in Table 3.4. It shows that both the moisture content and the volatile matter decreased with increase in temperature during process. The moisture content of biomass decreased from 6.18% (DAN) to 0.88% (TAN280-40). Besides, the volatile matter also decreased from 81.77% (DAN) to 36.84% (TAN280-40). Vassilev et al. (Vassilev et al., 2013) revealed that biomass having higher volatile matter is well suited for production of bio-oil through pyrolysis. The amount of volatile matter released from biomass depends on the temperature, retention time and heating rate during the process (Cai et al., 2017). It should be mentioned that the quantity of bio-oil could be reduced if TAN (low volatile matter) is pyrolyzed as compared to DAN (high volatile matter); however, the quality of bio-oil will be improved due to decreased O/C ratio as evident from Fig. 3.3. The ash content of biomass increased from 0.69% for DAN to 1.87% for TAN280-40. The fixed carbon increased from 11.35% for DAN to 60.40% for TAN280-40. The increase in fixed carbon and ash content of biomass was perceived after torrefaction since devolatilization of biomass increases with increase in temperature which results in relative decrease in moisture content and volatile matter and relative increase in fixed carbon and ash content of biomass. With increase in temperature, rate of release of light volatile matter (light hydrocarbon like methane, ethane, etc.) from biomass increases which affects the properties obtained from proximate analysis of biomass. During the torrefaction, release of hydrogen and oxygen in form of condensable liquid and gaseous products are more pronounced than release of carbon. The higher carbon content in biomass after torrefaction is accountable for increase in HHV of TAN. The higher heating values obtained for DAN, TAN220-40, TAN250-40, and TAN280-40 are 19.31, 20.77, 22.54, and 24.76 MJ/kg, respectively. Similar results for HHV were also obtained by Chen et al. (Chen et al., 2015c), Chen et al. (Chen et al., 2011) and Phanphanich et al. (Phanphanich & Mani, 2011) for same kind of biomass.

Table 3.4 Proximate and ultimate analysis of raw and torrefied biomass

Analysis	**DAN**	**TAN220-40**	**TAN250-40**	**TAN280-40**	**Coal sample[#]**
Proximate analysis (wt %)					
Moisture content	6.18	2.52	1.86	0.88	2.67
Ash content	0.69 (0.73)	1.24 (1.27)	1.39 (1.41)	1.87 (1.88)	6.63 (6.81)
Volatile matter	81.77 (87.15)	58.57 (60.08)	46.07 (46.94)	36.84 (37.16)	39.58 (40.66)
Fixed carbon*	11.35 (12.09)	36.66 (37.60)	50.66 (51.62)	60.40 (60.93)	51.12 (52.52)
Ultimate analysis (wt %)					
Carbon	43.84	50.31	58.62	64.75	76.48
Hydrogen	7.88	6.75	5.24	4.85	5.24
Nitrogen	0.42	0.63	0.69	0.64	2.32
Oxygen*	47.86	42.31	35.45	29.76	8.27
Sulphur	ND	ND	ND	ND	1.06
Higher heating value (MJ/kg)	19.31 (20.58)	20.77 (21.30)	22.54 (22.96)	24.76 (24.97)	30.42 (31.25)
Energy density ratio	-	1.19	1.11	1.05	-
Energy yield (%)	-	74.10	62.99	45.36	-

*Calculated by difference; ND Not detected; values in the parentheses are based on dry basis; # data for coal sample has been taken from (Shabbar & Janajreh, 2013).

The van Krevelen diagram may be used to compare the elemental composition of biomass with that of coal. In this diagram, the atomic ratio of hydrogen to carbon (H/C) is plotted against the atomic ratio of oxygen to carbon (O/C). Fig. 3.3 shows the van Krevelen diagram for DAN, TAN220-40, TAN250-40, and TAN280-40. As the temperature increases during torrefaction, the amount of oxygen and hydrogen present in biomass decreased with the relative increase in carbon content. The carbon content of DAN, TAN220-40, TAN250-40, and TAN280-40 is found to be 43.84, 50.31, 58.62, and 64.75 wt%, respectively. Thus, with increase in temperature during torrefaction the carbon content of resulting solid product increases. The increase in carbon content of TAN is attributed to higher heating value of TAN. However, the solid yield decreases with increase in temperature (Fig. 3.2). Therefore, a balance between carbon content of TAN and solid product yield should be established. Hence, torrefaction at 250 ℃ and 40 min retention time is considered optimum for further studies. In addition, properties of TAN also move towards the properties of coal suggesting that TAN may be used as a substitute of coal. The ICP-MS was performed to analyze the effect of torrefaction on the metal content of DAN. The results are presented in Table 3.5. In can be observed that TAN is enriched in Sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), aluminum (Al), nickel (Ni) and cobalt (Co) while some elements such as chromium, Zink, and beryllium were not detected. The concentration of detected elements increased with increase in temperature during torrefaction. Presence of elements in TAN might be responsible for higher reactivity of TAN than the DAN. Also, TAN may be used as an agent for soil amendment (Gupta et al., 2018; Mullen et al., 2010).

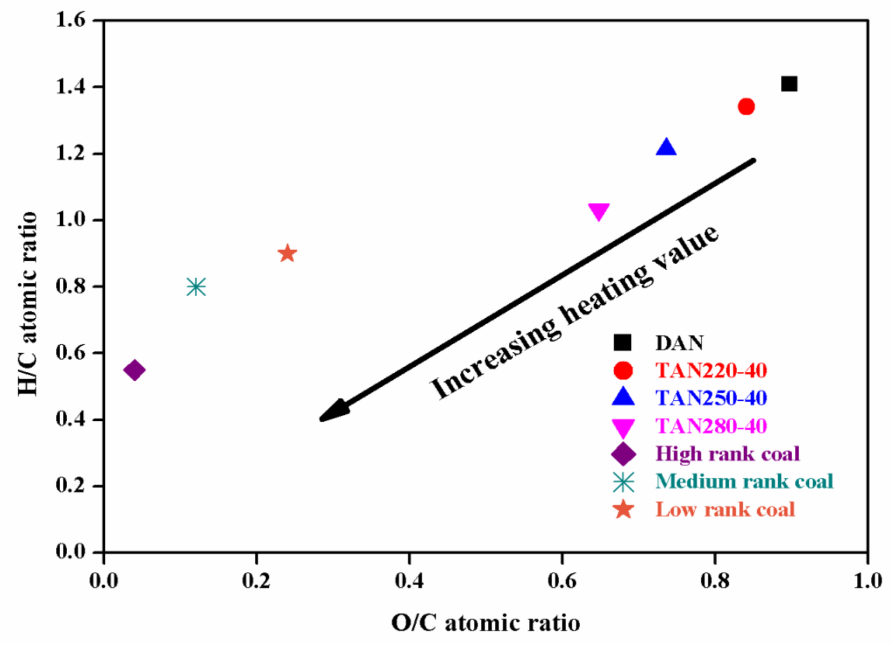

Figure 3.3 Van Krevelen diagram for raw and torrefied biomass

The range of CHO index can be from −4 to +4 (Cai et al., 2017). Higher value of CHO index depicts more oxidized compounds, while lower CHO index depicts reduced molecules of oxidized compounds. The CHO index obtained for DAN, TAN220-40, TAN250-40, and TAN280-40 are -0.34, -0.34, -0.55 and -0.58, respectively. The typical value of CHO index for biomass varies between -0.50 to + 0.05 (Cai et al., 2017; Mann et al., 2015). This index decreases with increasing temperature of torrefaction and are presented in Table 3.6. This clearly shows that the oxygen content of biomass decreases during this process. A positive value of CHO index for any biomass suggests that the amount of oxygen present in biomass is quite high (Cai et al., 2017; Mann et al., 2015).

Table 3.5 ICP-MS analysis of raw and torrefied biomass

Elements	**Concentration@ of elements in different sample**				
	DAN	**TAN220-40**	**TAN250-40**	**TAN280-40**	**Coal sample****
Na	219	238	316	387	209
K	29	45	88	142	974
Mg	107	122	176	284	252
Ca	642	880	1097	1864	1081
Al	27	32	73	155	6931
Fe	23	40	88	143	5591
Ni	3	4	4	8	9.8
Cr	ND	ND	ND	ND	11.7
Mn	2	2	3	5	12.3
Zn	ND	ND	ND	ND	12.5
Co	6	6	6	10	1.13
Be	ND	ND	ND	ND	0.52

@ Concentration of elements are presented in ppm; ND not detected; ** data for coal has been taken from (Balarama Krishna et al., 2015)

Color is an important parameter for biomass fuel, like the biomass having dark color, is known for its high ash content. The color of DAN and TAN indicates the severity of process. The color of treated biomass has a direct relation with its calorific value, darker the treated biomass higher will be the calorific value. Fig. 3.4 shows the physical appearance of DAN, TAN220-40, TAN250-40, and TAN280-40. It can be clearly observed that TAN obtained at higher temperature had darker color and higher calorific value. In industries associated with biomass, color can be a time-saving parameter to judge the quality of biomass by preventing lab scale testing of properties like moisture content, calorific value and hydrophobicity. Tooyserkani et al. (Tooyserkani et al., 2013) suggested that pellets made from bark of wood were darker in color.

Figure 3.4 Color appearance of raw and torrefied biomass

3.3.3 Density, porosity, and particle size raw and torrefied biomass

Three type of densities namely bulk, tapped and particle density and porosity of DAN and TAN were calculated using equations (3.5), (3.6), (3.7), and (3.8). Density is a key physical parameter for crafting a system for storage, handling, and transport of biomass. Bulk density of biomass varies with moisture content, particle dimension (size and shape), and surface morphology (Bhagwanrao & Singaravelu, 2014; S. Lam et al., 2008). The variation of density and porosity of DAN and TAN obtained at different temperature is given Table 3.6. Results showed that densities (bulk, tapped and particle) of DAN and TAN were reduced at higher process temperature, while, porosity of biomass increased due to removal of volatile content present in biomass. The porosity of DAN and TAN280-40) were 0.79 and 0.83, respectively. These results are well supported by the results obtained by Conag et al. (Conag et al., 2017) for bulk and tapped density of biomass.

Table 3.6 Fuel and flow properties, different types of densities of DAN and TAN

Properties	**DAN**	**TAN220-40**	**TAN250-40**	**TAN280-40**	**Coal sample**
Fuel properties/indices$^{\$}$					
FR	0.13	0.62	1.09	1.63	1.29
CI (MJ/kg)	147.40	38.99	24.67	17.37	24.96
VI (MJ/kg)	15.76	15.69	15.65	15.37	31.15
H/C	0.17	0.13	0.08	0.07	0.06
O/C	1.09	0.84	0.60	0.45	0.10
VM/FC	7.20	1.59	0.90	0.60	0.77
CHO index	−0.34	−0.34	−0.55	−0.58	-
Flow properties$^{\$\$}$					
Angle of repose (°)	39.36	38.79	36.15	32.51	36.8
HR	1.29	1.27	1.21	1.18	1.10
CCI	22.85	21.44	17.35	15.86	9.23
C	0.40	0.39	0.36	0.33	0.28
Bulk density (kg/m^3)	230.82	210.34	190.18	172.84	727
Tapped density (kg/m^3)	299.21	267.77	230.13	205.43	801

Particle density (kg/m^3)	1220	1150	1110	1050	1500
Porosity	0.81	0.81	0.82	0.83	-
Particle size (mm)	0.50	0.48	0.46	0.45	-

$ data for fuel properties of coal has been taken from (Shabbar & Janajreh, 2013); $$ data for flow properties of coal has been taken from (Lu et al., 2015).

The dimensions (size and shape) of biomass particles have significant consequence on the mixing, fluidization, and surface area. It also affects the heat and mass transfer along with flow behavior of biomass particles. Hence, the thermochemical process involving various dimensions of biomass can have different efficiency and energy requirement. The particle size of biomass feedstocks highly affects the thermochemical conversion process. Generally biomass has irregular shape and size which creates difficulties in the precise measurement of dimension (length, width, and thickness). The precise description of biomass dimension is crucial for processing, handling, and storage. Sieve analysis is a major technique for characterization of particle size (geometric mean diameter) of DAN and TAN. According to Eqs. (3.10), the geometric mean diameters of DAN, TAN220-40, TAN250-40, and TAN280-40 are found to be 0.50, 0.48, 0.46 and 0.45 mm, respectively. The screen analysis of DAN, TAN220-40, TAN250-40, and TAN280-40 is shown in Fig. 3.5 (a) and (b). It was observed that at higher temperature during torrefaction the fraction of smaller particle increases and uniformity in the particle size was obtained. Smaller particle obtained after torrefaction have lower heat resistance in further thermochemical process. Based on the results of screen analysis, SEM analysis, and density of TAN, it may be predicted that comminution of TAN becomes easier than the DAN. SEM analysis revealed that tenacious and fibrous structure of biomass is removed after torrefaction and pores were seen on the surface of biomass. Based on this observation, it may be noted that comminution of TAN is likely to be less energy-intensive process. In addition, decrease in density of biomass after torrefaction also favors easier comminution of TAN. Similar finding were reported by Arias et al. (Arias et al., 2008b), and Tumuluru et al. (Tumuluru & Heikkila, 2019). Tumuluru et al. (Tumuluru & Heikkila, 2019) optimized the grinding process using response surface methodology taking moisture content and grinder speed as input variables. They reported that at constant grinder speed of 20 Hz, specific grinding energy (kWh/ton) requirement would be lowered by 39.1 % if the moisture content was reduced from 20 wt% to 10 wt %. In the present work the moisture content for TAN220-40, TAN250-40, and TAN280-40 was decreased by 59.22, 69.90, and 85.76 %, respectively, as compare to the native biomass (DAN). Based on these observations, it can be mentioned that the comminution of TAN may be easier than that of DAN. Fig. 3.5 (b) shows the cumulative mass (wt%) retained on the screen and it was observed that mass of uniform particle size on each screen is obtained in case of TAN in contrast to DAN having unequal proportion of biomass on each screen. The larger biomass particle offers larger mass transfer and heat transfer resistance.

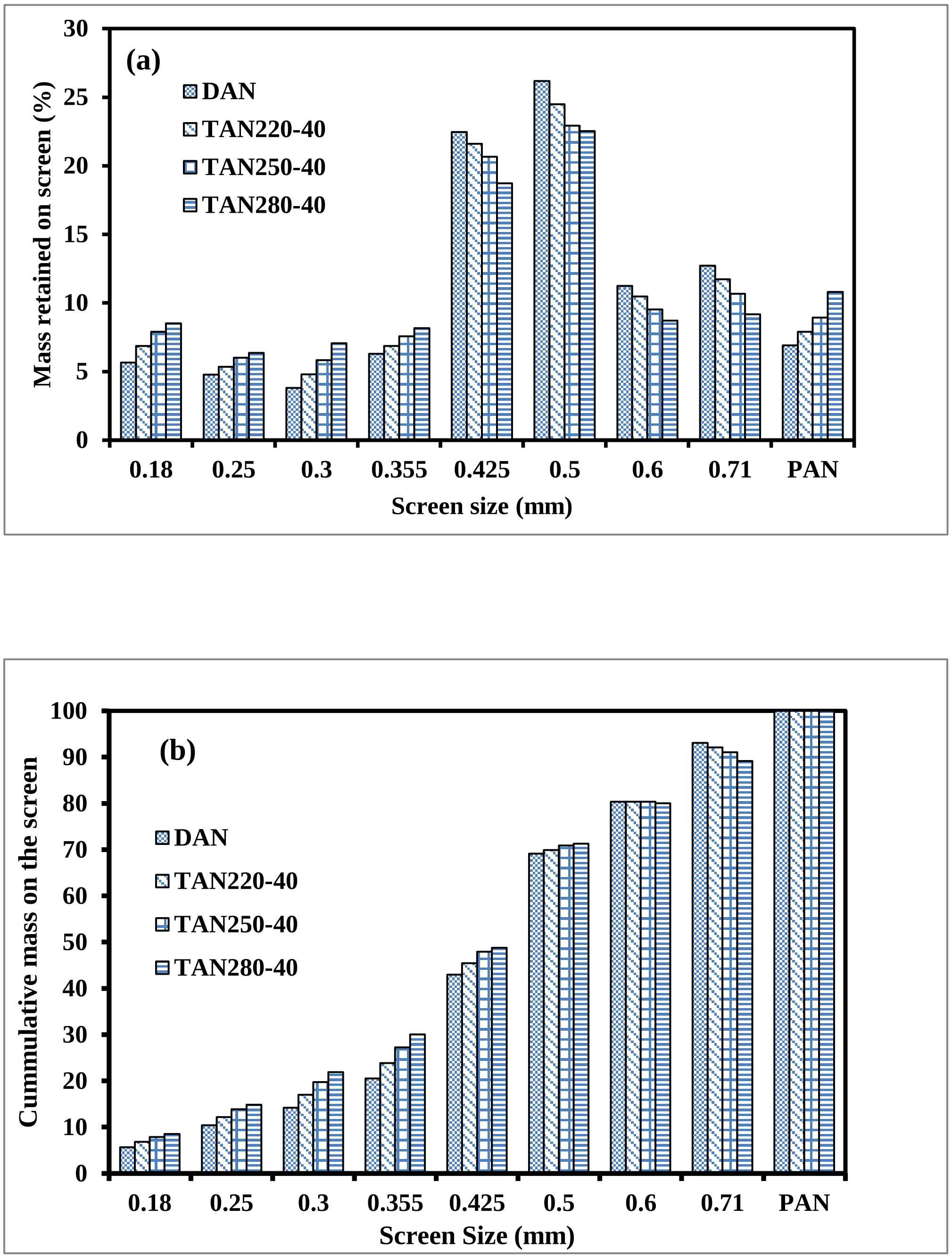

Figure 3.5 (a) Particle size distribution of raw and torrefied biomass **(b)** Cumulative mass distribution for raw and torrefied biomass

3.3.4 Moisture sorption characteristics of raw and torrefied biomass

The biomass has hydrophilic characteristics due to which it absorbs moisture when kept in open environment which causes biological degradation. Major constituents of biomass are hemicellulose, cellulose, and lignin. Each of these components contain hydroxyl group (-OH). Due to presence of this hydroxyl group biomass forms hydrogen bond with moisture, which makes it hygroscopic in nature. This higher moisture content in the biomass is undesirable since it leads to low energy efficiency, high energy loss, and higher emission when the biomass is used in thermochemical conversion process along with higher transport, storage and handling cost (Bach & Skreiberg, 2016).

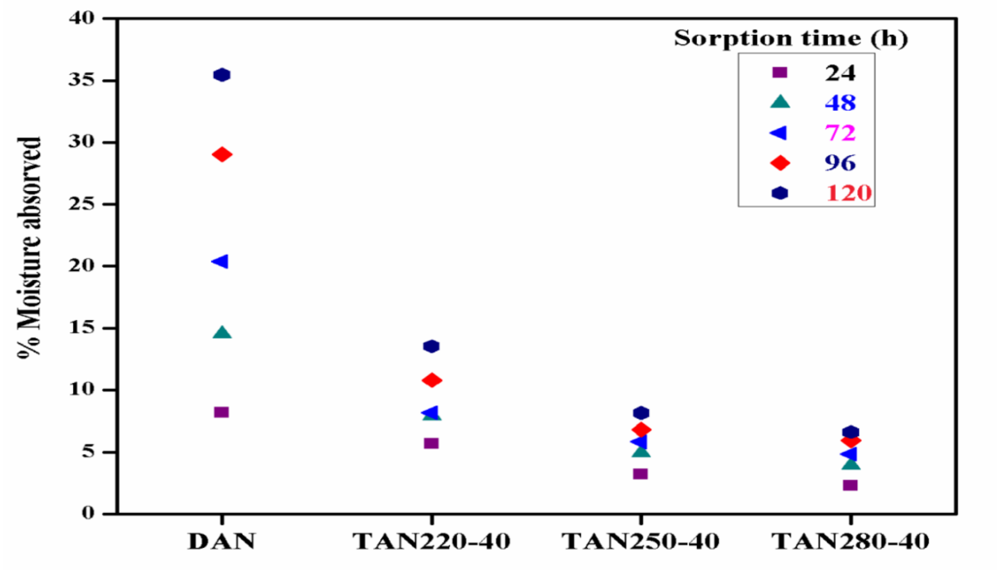

Figure 3.6 (a) Moisture sorption test of raw and torrefied biomass in open environment

Fig. 3.6 (a) shows the percentage of moisture absorbed in DAN and TAN220-40, TAN250-40, and TAN280-40. After five days, percentage of moisture absorbed by DAN, TAN220-40, TAN250-40, and TAN280-40 is 35.44%, 13.52%, 8.15% and 6.61% respectively. The torrefaction of biomass makes it hydrophobic in nature so that it absorbs minimal amount of moisture and becomes more stable when stored in an open environment. During torrefaction, hydroxyl group (-OH) associated with biomass is ruptured resulting in lower affinity of biomass to associate with water through hydrogen bonding (Bach & Skreiberg, 2016). Torrefaction makes the biomass unsaturated which have non-polar properties. In addition, the tar present in the liquid condensate might get condensed on the surface and block the pores present in the TAN which can further reduce the water absorption capacity of TAN through capillary action (Ohm et al., 2015)**.** This implies that the torrefaction can improve the logistic characteristics of biomass. The hydrophobic nature of TAN was also confirmed by contact angle measurement. For hydrophobic character the value of contact angle should be close to 90° (Strandberg et al., 2015). Fig. 3.6 (b) shows the contact angle of DAN and TAN. The contact angle from left and right side of the meniscus for DAN, TAN220-40, TAN250-40, and TAN280-40 was found to be 46.5-47.8°, 64.9-64.3°, 70.3-70.1° and 79.9-77.5° respectively. Thus, it can be concluded that hydrophobic characteristics of biomass increases with increase in temperature during torrefaction.

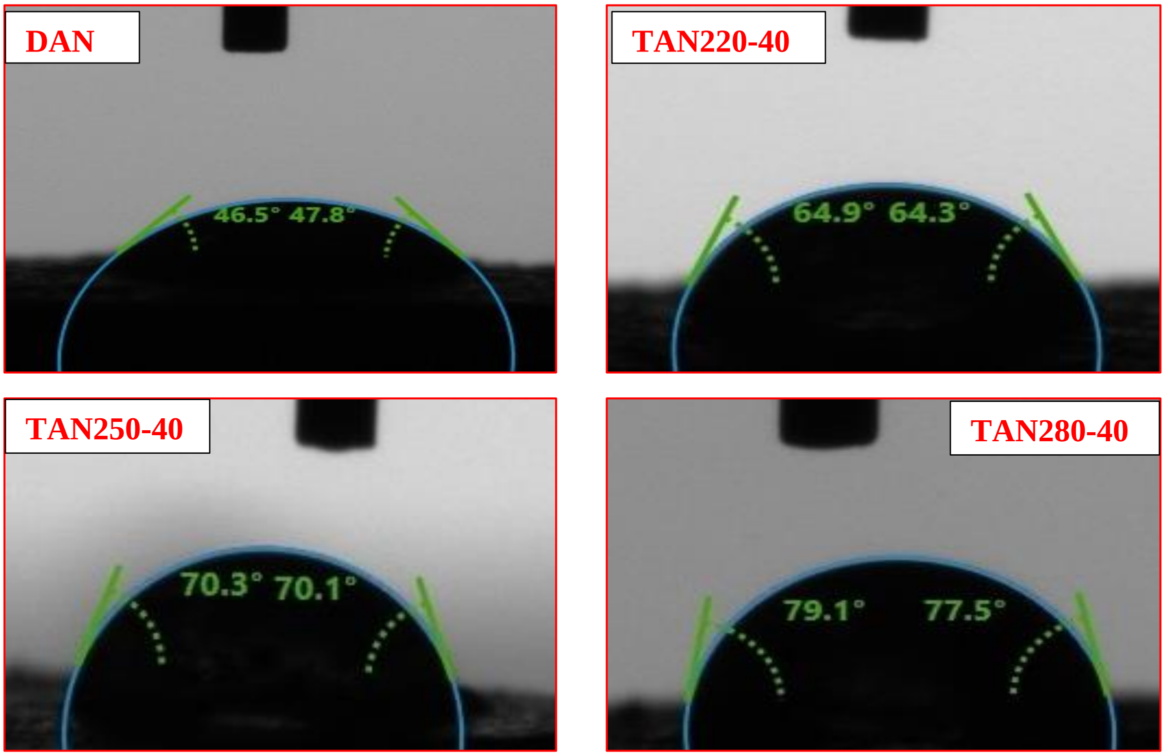

Figure 3.6 (b) Moisture sorption test of raw and torrefied biomass using contact angle measurement

3.3.5 Flowability of raw and torrefied biomass

Flowability is the property of biomass which depicts the ease of motion of biomass from one point to other during the process. The flowability is an important characteristic of biomass which plays a crucial role during its utilization in conversion and co-conversion processes. The flow characteristics of DAN and TAN are shown in Table 3.6. The flow behavior of DAN and TAN based on Hausner ratio (HR), cohesion coefficient (C), Carr compressibility index (CCI) and angle of repose were analyzed and compared from Table 3.7 obtained from literature. The angle of repose for DAN, TAN220-40, TAN250-40, and TAN280-40 are 39.36, 38.79, 36.15, and 32.51 respectively. The calculated value of

Hausner ration in this work for DAN, TAN220-40, TAN250-40, and TAN280-40 are 1.29, 1.27, 1.21 and 1.18, respectively, while, Carr compressibility index of DAN, TAN220-40, TAN250-40, and TAN280-40 are 22.85, 21.44, 17.35 and 15.86, respectively. The cohesion coefficient of DAN, TAN220-40, TAN250-40, and TAN280-40 are 0.40, 0.39, 0.36, and 0.33, respectively. During the course of torrefaction, solid product obtained at higher temperature has lower angle of repose and has better flowing property than the DAN.

Table 3.7 Characteristic flow properties of biomass (Lumay et al., 2012; Szalay et al., 2015)

Flow property	Angle of repose (degree)	Hausner ratio (HR)	Carr compressibility index (CCI)
Excellent	25-30	1.00-1.11	≤ 10
Good	31-35	1.12-1.18	11-15
Fair	36-40	1.19-1.25	16-20
Passable	41-45	1.26-1.34	21-25
Poor	46-55	1.35-1.45	26-31
Very Poor	56-65	1.46-1.59	32-37
Very very Poor	>66	>1.60	>38

The TAN at a higher temperature has better flowing property than DAN or low temperature torrefied material. The Carr compressibility index of DAN, TAN220-40, TAN250-40, and TAN280-40 are 22.85, 21.44, 17.35 and 15.86 respectively. The TAN at higher temperature has lower tendency to agglomerate resulting in better flow behavior in comparison to DAN. Cohesion coefficient signifies the cohesive and frictional force of biomass particles (Szalay et al., 2015). The cohesion coefficient of DAN, TAN220-40, TAN250-40, and TAN280-40 are 0.40, 0.39, 0.36, and 0.33, respectively, which revealed that cohesive force in case of TAN is lower than the DAN resulting in better flow behavior of TAN as compared to DAN.

3.3.6 Combustion indices of raw and torrefied biomass

Table 3.6 presents the combustion indices of DAN and TAN. The combustion indices are generally used to define quality of torrefied biomass after thermochemical conversion processes. Fuel ratio (FR), combustibility index (CI), and volatile ignitability (VI) are determined using equations (1.5), (1.6), and (1.7), respectively. The fuel ratio of DAN increased after torrefaction due to increase in fixed carbon and simultaneous decrease in volatile content of biomass. In case of coal, the recommended range for fuel ratio is 0.5-3.0. The TAN obtained at 280 ℃ and 40 min retention time having the fuel ratio 1.63 which makes it suitable for firing in power plants along with coal. The higher fuel ratio causes an incomplete burning of fuel which reduces the efficiency of boiler when such fuel is used during its operation. During the process, the fuel with a fuel ratio greater than two may cause problems with ignition and flammability. The published combustibility index and volatile ignitability ranges are: combustibility index should be below 23MJ/kg and volatile ignitability should be above 14.5MJ/kg (Ohm et al., 2015). The value of combustibility index and volatile ignitability of DAN are 147.40 MJ/kg and 15.76 MJ/kg, respectively. It means that, without prior treatment DAN cannot be suited as an alternative energy source. The calculated value of combustibility index for TAN220-40, TAN250-40, and TAN280-40 are 38.99, 24.67, and 17.37 MJ/kg, respectively. The calculated value of

VI for TAN220-40, TAN250-40, and TAN280-40 are 15.69, 15.65, and 15.37 MJ/kg, individually. Similar kind results were obtained by Singh et al. (Singh et al., 2019a). It shows that TAN obtained at 280 ℃ has nearly comparable characteristics like coal, and it can be used as a substitute source of energy and also, TAN can be blended with coal.

3.3.7 Thermogravimetric analysis

Fig. 3.7 (a) shows the thermogravimetric analysis of DAN and TAN. The plot revealed that, in case of TAN, fixed amount decomposition attained at higher temperature. For DAN, mass loss of 20% was attained at 280 ℃, however, the same amount of mass loss was observed at 336, 351, and 496 ℃ in case of TAN220-40, TAN250-40, and TAN280-40, respectively. This shifting of decomposition temperature for TAN might be due to breakdown of hemicellulose and retaining most of the cellulose and lignin. The different components of biomass have range of temperature for thermal decomposition. Hemicellulose and cellulose, generally decomposed at between 200-350 ℃, while lignin decomposed between 280-600 ℃ (Ren et al., 2013a). For hemicellulose and cellulose, substantial weight loss was observed from 268 ℃ to 355 ℃ (Yang et al., 2007). The DTG curve of DAN and TAN are presented in Fig. 3.7 (b). At around 300 ℃, a shoulder in DTG curve of biomass corresponds to degradation of hemicellulose (Müller-Hagedorn et al., 2003; Yang et al., 2007). In present work similar kind of shoulder is appeared in case of DAN Fig. 3.7 (b). However, in case of TAN220-40, TAN250-40 and TAN280-40, the shoulder cannot be observed, which revealed that the hemicellulose of DAN has decomposed in course of torrefaction. In DTG curve, the peak associated with maximum mass loss corresponds to cellulose content of biomass (Yang et al., 2007). Around 340 ℃, similar peaks attributed to cellulose can be perceived in case of DAN and TAN which signifies lesser decomposition of cellulose in comparison to hemicellulose during torrefaction. However, intensity of peak for TAN decreases as the temperature increases during the process.

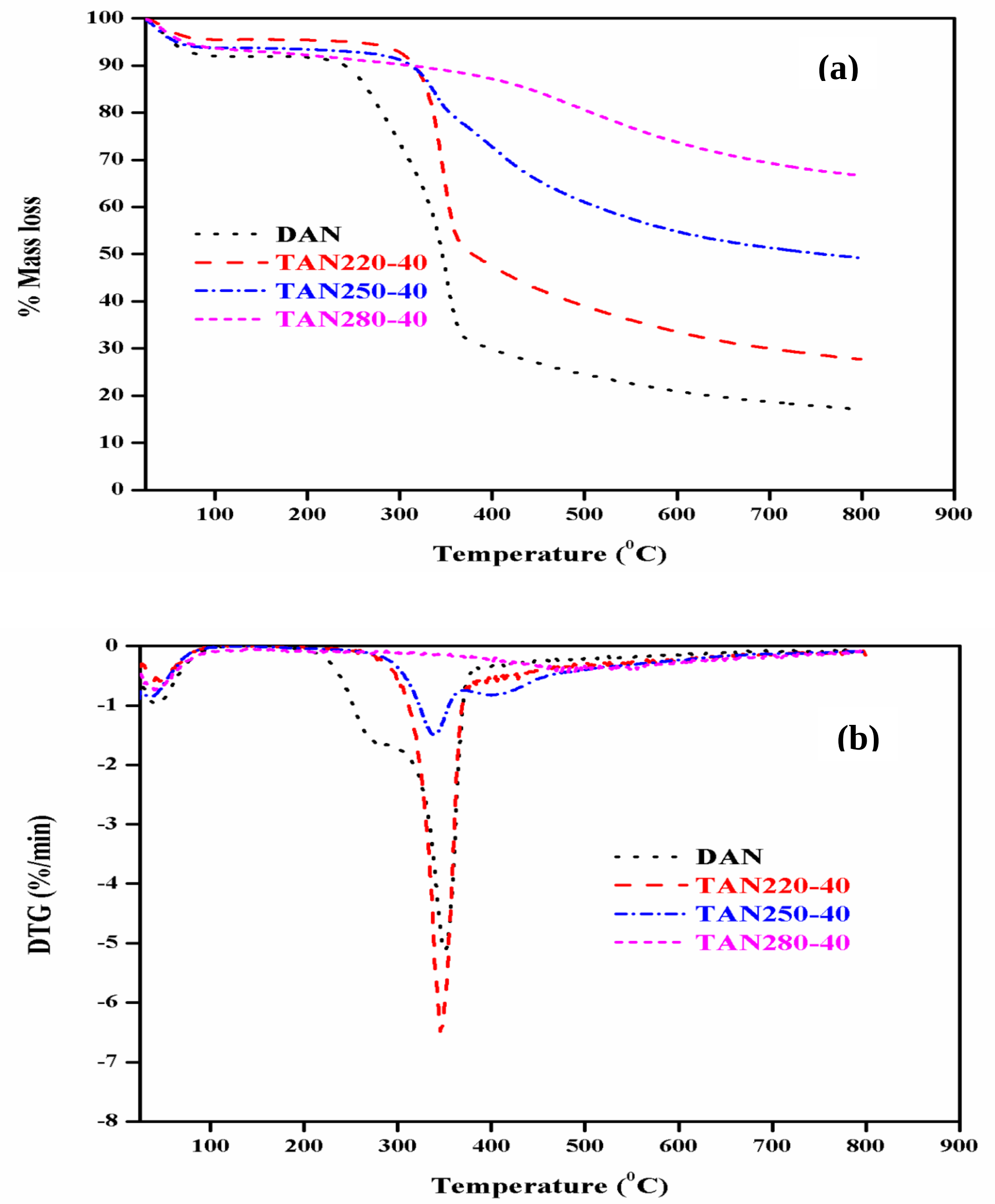

Figure 3.7 Thermogravimetric analysis of raw and torrefied biomass (a) TGA analysis (b) DTG analysis

3.3.8 FTIR analysis of raw and torrefied biomass

The analysis of various chemical functional groups present in DAN and corresponding changes in then after torrefaction was analyzed by employing Fourier transform infrared spectroscopy (FTIR) (Fig. 3.8). The breakdown of hemicellulose during torrefaction is mainly accountable for alteration in chemical structure of DAN. The distinctive peak among 3300-3100 cm^{-1} ascribed the stretching vibration of hydroxyl group (-OH) associated with hemicellulose of biomass. It also confirmed the hydrogen bond present between alcohol and phenol groups associated with hemicellulose and cellulose component of biomass (Min et al., 2011). Decrease in intensity from 3300-3100 cm^{-1} waveband inferred the breaking of hydrogen bond present between alcohol and phenol. This increases the durability of biomass against the moisture and biological attacks along with make it suitable for long storage, easy handling, and transportation.

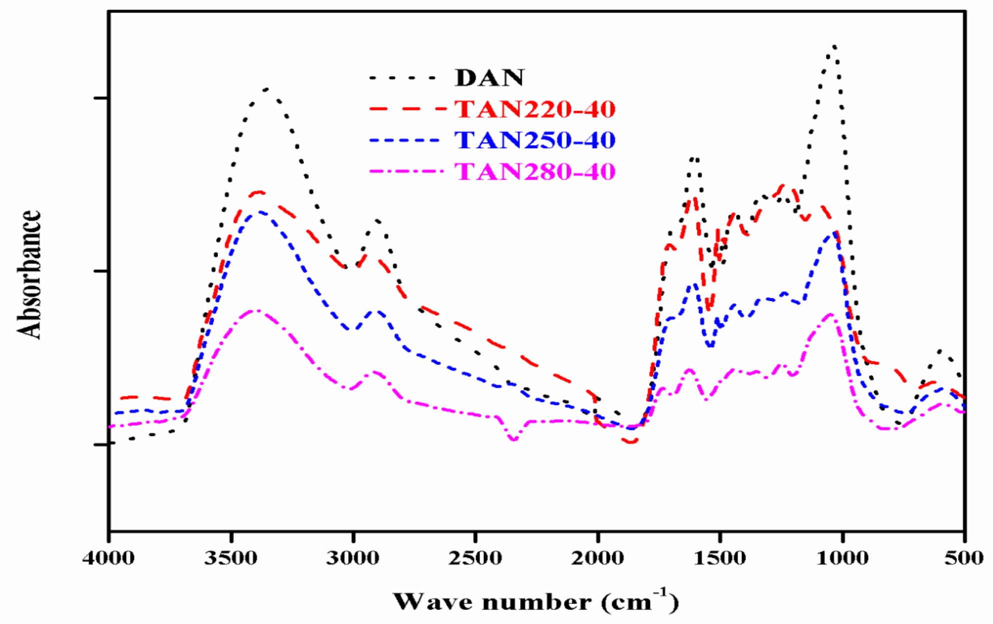

Figure 3.8 FTIR analysis of raw and torrefied biomass

The specific peaks between 2900-2750 cm^{-1}, 1750-1500 $cm^{-1,}$ and 1200-1000 cm^{-1} were observed due to stretching vibration in C=O bond, C=C bond, C-H bond, and C-O-C bond respectively (Azargohar et al., 2014; Keiluweit et al., 2010; Sharma et al., 2001).With increase in temperature during torrefaction, the in intensity of peaks reaffirming the rupture of chemical bonds such as C=O, C-O-C, CHO- etc. present in the biomass. Reduction in peak intensity from 1750-1500 cm^{-1} corresponds to cleavage of ester group associated with hemicellulose through deacetylation reaction (Carrasco & Roy, 1992). The characteristic peak between wavenumber 600-700 cm^{-1}, attributed to existence of aromatic compounds with mono and cyclic groups (Gomez-Serrano et al., 1996).

3.3.9 SEM-EDX analysis of raw and torrefied biomass

The scanning electron microscopy (SEM) analysis of DAN, TAN220-40, TAN250-40 and TAN280-40 at 2K magnification is depicted in Fig. 3.9 to investigate the impact of torrefaction on biomass morphology. The effect of torrefaction could be clearly perceived in Fig. 3.9 (c), (e), and (g). Hemicelluloses are typically branched polysaccharides comprising solid bulky and branched xylem tissues (Ibrahim et al., 2013). Hemicellulose is elucidated by a branched arrangement associated with the DAN. Nevertheless, in the case of TAN, this branched structure began to disappear, indicating hemicellulose degradation during torrefaction (Fig. 3.9 (c), (e), and (g)). The formation of pores is visible for TAN220-40, TAN250-40, and TAN280-40. An increase in the pore size with increasing temperature could be seen from Fig. 3.9 (g) where the biomass was torrefied at 280 ℃ for 40 min. The appearance of pores on the surface of TAN was ascribed its lower density than the DAN which can increase the surface area and lower grinding energy as compared to DAN. Ibrahim et al. (Ibrahim et al., 2013), and Bach et al. (Bach & Skreiberg, 2016) mentioned the similar kind of results. Along with SEM analysis, energy dispersive X-ray (EDX) was also performed to identify elements present on the surface of DAN and TAN. EDX images of DAN, TAN220-40, TAN250-40, and TAN280-40 are depicted in Fig. 3.9 (b) (d) (f) and (h), respectively. The results revealed that with increase in severity of the torrefaction process, peaks corresponding to nitrogen, calcium, magnesium and potassium are appearing in TAN220-40, TAN250-40, and TAN280-40 with high intensity. However, in case of DAN, only carbon, oxygen and potassium can be seen. Presence of these elements in the TAN makes it suitable for soil amendment to increase the fertility of soil (Gupta et al., 2018; Mullen et al., 2010).

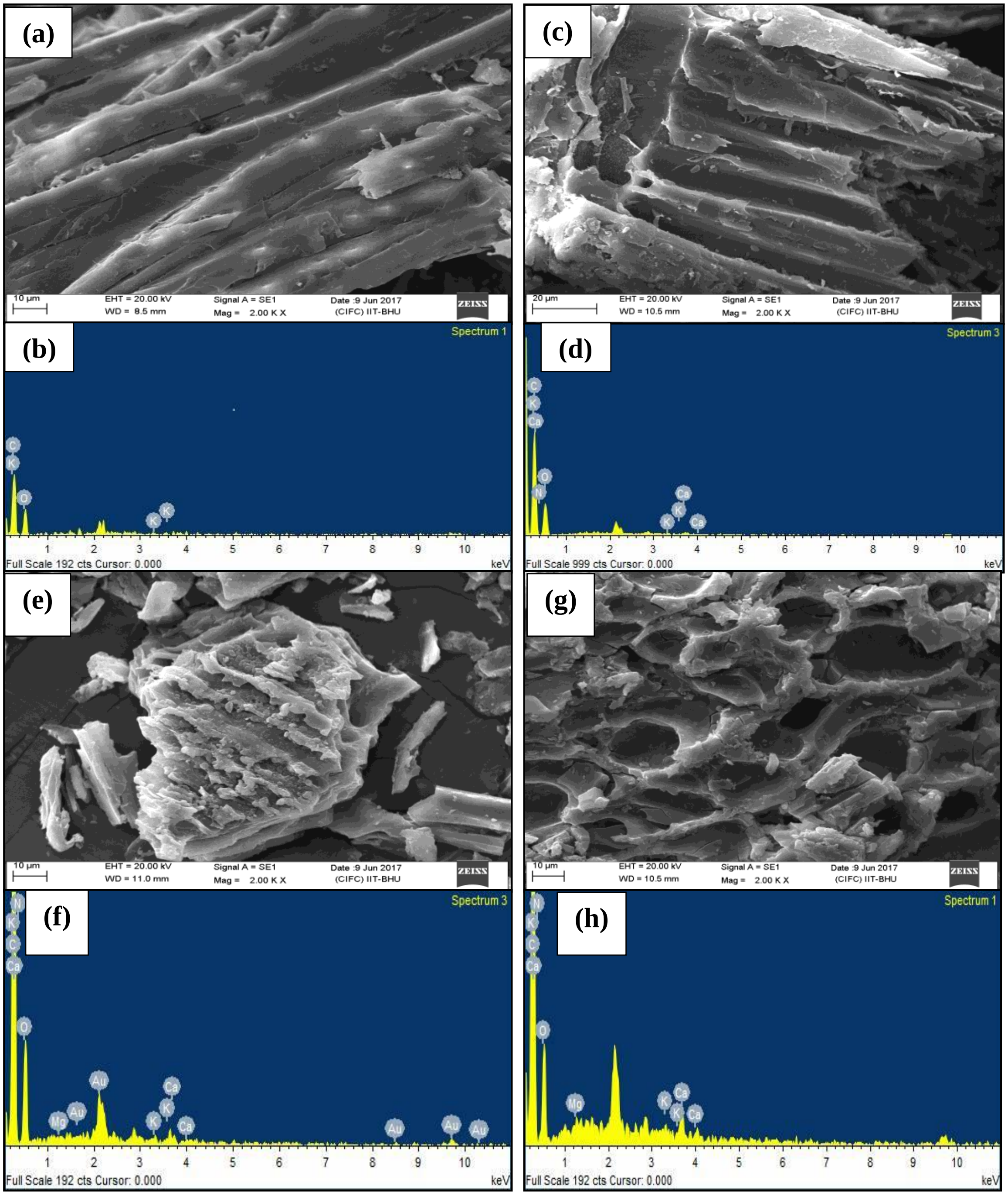

Figure 3.9 SEM and EDX images of raw and torrefied biomass: (a) and (b) DAN, (c) and (d) TAN220-40, (e) and (f) TAN250-40 and (g) and (h) TAN280-40

3.4. Conclusions

Experimental investigation of torrefaction of *Acacia nilotica* within a temperature range of 220- 280 ℃ and retention time between 20-60 min was performed. Various properties which validate good quality of solid fuel from biomass were examined. Results showed that temperature during torrefaction had more pronounced effect on solid yield as compared to retention time. Fuel and flow characteristics of *Acacia nilotica* has been improved after torrefaction and are closure to the properties of coal. The higher heating value (HHV) increased by 28.2 % when DAN was torrefied at 280 ℃ for 40 min. TAN was found to be less hygroscopic as moisture reabsorbed was 6.61 % (TAN280-40, 120 h) as compared to 35.44 % (DAN, 120 h). Also, the contact angle of TAN280-40 (79.1°/77.5°) was close to 90° confirming the hydrophobic nature. The bulk density of TAN was suitable for use as briquette and co-firing with coal in thermal plants with HR value less than 1.29 and CCI less than about 23. There was significant decrease in volatile matter (57.4 %) with simultaneous increase in fixed carbon content (~4 times). Hence, less volatile matter and high fixed carbon make TAN a better solid fuel. TGA results showed that devolatilization temperature shifted to higher value and residual char yield increases when TAN was pyrolysed. ICP-MS analysis revealed that TAN enriched by important elements such as sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) etc. making it suitable for soil amendment. Finally, *Acacia nilotica* exhibited better performance as compared to other woody biomass because of enhanced HHV, low ash content etc.

Chapter 4

Intrinsic kinetics, thermodynamic parameters and reaction mechanism of non-isothermal degradation of torrefied *Acacia nilotica* using isoconversional methods

General background

This chapter aimed to examine the suitability of torrefied *Acacia nilotica* for bio-energy generation by investigating its kinetic and thermodynamic parameters as well as reaction mechanism during pyrolysis based on thermogravimetric analysis. Thus, torrefaction of *Acacia nilotica* was performed in a fixed bed reactor at 220, 250 and 280 ℃, with constant retention time (40 min) and heating rate (15 ℃/min). Pyrolysis of dried *Acacia nilotica* (DAN), torrefied *Acacia nilotica* obtained at 220 ℃ (TAN220), 250 ℃ (TAN250) and 280 ℃ (TAN280) was performed using thermogravimetric analyzer at three different heating rate viz. 5, 10 and 15 K/min. Further, isoconversional models namely, Kissinger-Akahira-Sunose (KAS), Ozawa-Wall-Flynn (OWF), Friedman and Starink were employed to calculate the kinetic parameters (activation energy and pre-exponential factor) of DAN and TAN. Using kinetic parameters obtained from KAS method, thermodynamic parameters (enthalpy, Gibbs free energy, and entropy) were calculated at a heating rate of 10 K/min. Reaction mechanism during pyrolysis of DAN and TAN was predicted using Criado method (Z-master plot).