

INVESTIGATION ON INDIGENOUS BIOMASS FEEDSTOCK UPGRADATION AS SOLID FUEL



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ABSTRACT

Biomass, a lignocellulosic material, has a potential to act as an alternative solid fuel in the energy generation processes and offers a viable solution for energy shortfall in developing countries as it is cheap source and easily available. However, some of the raw biomass inherent properties, such as high moisture content, slagging nature, low mass and energy densities which hinder its commercial utilization. Among various proposed pretreatment solutions, demineralization and torrefaction are promising pretreatment processes for converting raw biomass into an efficient and suitable solid fuel. In demineralization process, minerals causing slagging are leached out of biomass using different acid solutions and torrefaction, also known as slow pyrolysis, is defined as the thermolysis of agricultural residue in the temperature range of 200-300 °C while maintaining an inert environment to improve its higher heating value (HHV) and hydrophobic nature.

Different leaching agents, including HCl and H₂SO₄, were used for the demineralization of the biomass with varying residence time. After the acid treatment, HHV of the agricultural residue increases and ash content decreases. The specimen leached with 5 wt. % H₂SO₄ solution with 120 min residence time showed 7.10% improvement in HHV and its ash content was decreased by 34.20% when compared to raw biomass. The demineralized samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). A slight change in the peak intensities of O-H, C-H, C=O and C=C stretching vibrations was noted through FTIR. The increased surface erosion and fuzziness through SEM confirms that few particles were leached away by the acid solutions. The shifting of shoulders in the thermal degradation (DTG) curve towards high temperature indicated that the treated specimen are showing more resistance towards their thermal degradation.

Torrefaction was performed to assess the improvement in the elemental composition, hydrophobic behavior and HHV of the biomass. The carbon content of thermolyzed biomass was raised to 48.46% from 32.45%. The hydrogen and oxygen contents showed a decline thus improving the hydrophobic behavior as higher oxygen content increases the moisture adsorption capability of the biomass and reduces its shelf life. The water uptake of torrefied samples decreased 92% from 307% due to which the ignition temperature of the treated samples reduces and stability and durability increases. The calorific value of the treated samples was also increased to 4913 cal.g⁻¹ compared to raw biomass having HHV 3939 cal.g⁻¹. The torrefied samples were also characterized by SEM and FTIR to observe the physio-chemical changes and surface morphology and their thermal degradation was also studied. The results confirmed that the most affected fraction of the lignocellulosic material is hemicellulose.

Torrefaction of the acid treated samples was also studied to evaluate the fuel properties of the specimen. For assessment of compositional changes, X-ray Fluorescence (XRF), ultimate and proximate analysis were performed. The XRF analysis confirms the removal of alkali and alkaline earth metals (AAEM) thus reducing the slagging nature of treated samples. The pretreatment processes upgrade the carbon content from 32.45% to 43.10%, hence also improved the HHV from 3939 cal.g⁻¹ to 4356 cal.g⁻¹. The reduction in the oxygen and hydrogen content is observed from 45.92% to 36.08% and 5.44% to 4.30%, respectively which improves the hydrophobic behavior as water uptake of the treated samples reduces by 55%.

LIST OF PUBLICATIONS

A list of publications produced as a result of this research work is given below.

JOURNAL PUBLICATION

- **Umair Aslam**, Naveed Ramzan, Tanveer Iqbal, Mohsin Kazmi and Aamir Ikhtlaq, “Effect of demineralization on the physiochemical structure and thermal degradation of indigenous rice husk”, Polish Journal of Chemical Technology, 18, 3, 117-121.
- **Umair Aslam**, Naveed Ramzan, “Enhancement of fuel characteristics of rice husk using torrefaction process” is under review in International Journal of Green Energy.
- **Umair Aslam**, Naveed Ramzan, “Impacts of demineralization and torrefaction on fuel characteristics of biomass” is in process.
- **Umair Aslam**, Naveed Ramzan, “Effect of pretreatments on thermal degradation behavior of biomass” is in process.

CONFERENCE

- “Energy densification of biomass using torrefaction” presented at 2ND International Conference on Chemical Engineering, held in Mehran University of Engineering and Technology, Jamshoro, Pakistan on January 22, 23 2018.
- “Physio-chemical evaluation and thermal degradation study of torrefied biomass” presented at 3rd International Conference on Engineering Sciences, held in PU and UET Lahore, Pakistan on December 21, 22 2017.
- “Upgradation of biomass feedstock as solid fuel” presented at 6th Symposium on Engineering Sciences held in PU and UET Lahore, Pakistan on December 21, 22 2016.

- “Biomass upgradation as solid fuel: issues and their solutions” (Poster) presented at 1st International Conference on Emerging Technologies for Waste Water Processes and Alternative Energy Resources held in University of Gujrat, Pakistan on June 1, 2 2016.

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CHAPTER 1: INTRODUCTION

1.1 Introduction

In the past few decades, the earth's climate has changed drastically. The emission of greenhouse gases (GHGs) is one of the key factors causing this change [1]. In an intergovernmental panel on climate change (IPCC) report, it is stated that in the last decade GHGs emission into the environment are the highest in the history [2]. Among various GHGs, carbon dioxide (CO₂) is the main gas causing a strong effect on the climate of earth and it is emitted into the atmosphere by the combustion of fossil fuels in power plants, process industries (fertilizer industries and refineries) and vehicles. The temperature of the earth is rising due to the global warming and CO₂ emission is considered as the main reason for the temperature increase [3].

The increase in population and electricity demand, and deforestation are the key factors causing the rise in GHGs emission, especially CO₂. The electricity demand will increase in excess of 75% by 2030 [4]. In 2008, US generated 68% electricity from fossil fuels, 9% from hydropower, 21% from nuclear power and 2% from renewable resources (solar and wind) [5]. The consumption of fossil fuels in power generation is the source of many concerns in areas of the environment, their availability (as the reserves are depleting) and development of the country. It is perceptible that renewable energy (RE) must be effectively utilized to reduce the dependence on fossil fuels. The RE is the energy which is derived from the resources replenished by the nature continually such as sunlight, wind, rain, geothermal heat, biomass, waves and tides [6].

The inclusion of indigenous RE sources could be a promising solution while tackling the problems of the global warming, energy shortfall and climate change specially in the developing countries like Pakistan. As shown in Figure 1.1, Pakistan is generating 87.00% of its total energy from the fossil fuel, majorly from the burning of oil (43%) and other sources respectively. The contribution

of the RE in the Pakistan's energy mix is negligible. The dependency on fossil fuel has increased the financial burden on country economy and raised the CO₂ emission level as well. At the same time, high prices of fossil fuel reduced the quantity of oil purchased, therefore, electricity could not be supplied as per demand [7]. Pakistan is currently facing an electricity shortfall of around 6000 MW [8]. The energy crisis in the country had coerced many industries (fertilizer, textile and leather industries) to shut down thus affecting the industrial production and livelihoods of the people [9–11]. The dependence on fossil fuel is unviable in long run and RE must be infiltrated into power generation.

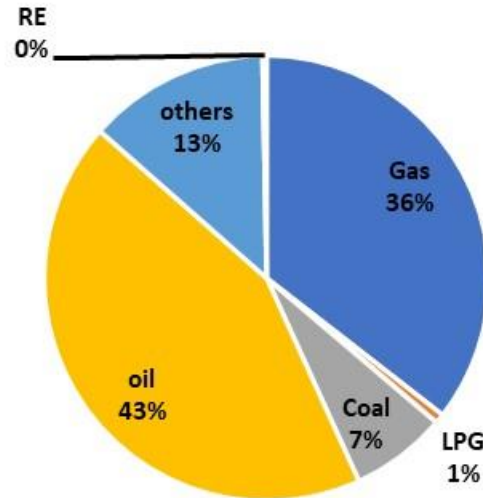


Figure 1.1: Pakistan's energy supply [11]

Being an agricultural country, nearly 62% of the country's population resides in rural areas, and is directly or indirectly linked with agriculture for their livelihood. Table 1.1 shows that Pakistan has a substantial bio resource base as annual production of agricultural residues is approximately 100 million tons, however the contribution of the bio resource to useful energy production is very low [12]. The generation of energy from RE has cost disadvantages when compared with non-

renewable fossil fuel but the increasing prices of fossil fuel in Pakistan, their depletion and the abundant availability of biomass residues may help in addressing the energy crisis [12-13].

Table 1.1: Production of different crops and their respective residue availability in Pakistan [11]

Name of the crop	Annual production (thousand metric ton, MT)	Type of residue	Crop to residue ratio (residue/kg crop)	Total available residue (thousand metric ton, MT)
Rice	6883.00	Husks	0.20	1376.60
		Stalks	1.50	10324.50
		Straws	1.50	10324.50
Cotton	3000.00	Boll shell	1.10	3300.00
		Husk	1.10	3300.00
		Stalks	3.80	11802.80
Wheat	23864.00	Pod	0.30	7159.20
		Stalks	1.50	35796.00
Sugarcane	49373.00	Bagasse	0.33	16293.09
		Top and Leaves	0.05	2715.52
Maize	296.00	Cobs	0.30	88.80
Bajra	470.00	Stalks	2.00	592.00
		Cobs	0.33	151.18
		Husks	0.30	141.00
Barley	82.00	Stalks	2.00	940.00
		Stalks	1.30	106.60
Dry chilly	187.70	Stalks	1.50	281.55

Biomass, a lignocellulosic material and RE source, could be a good alternative energy resource as it can be utilized in three forms, such as gaseous (biogas, producer gas), liquid (biodiesel, ethanol) and solid (char, pellet, briquette) [15]. It is the only renewable source that carries sustainable carbon as CO₂ produced from biomass combustion is utilized by the cultivation of new crops [16]. Three major constituents of biomass are cellulose, hemicellulose and lignin. Hemicellulose, a polysaccharide, consists of smaller chains (500-3000 sugar units) and it accounts for about 25-30 wt% of biomass [17]. The structure of hemicellulose is shown in Figure 1.2. It has different

monomers in different woods and plants. The thermal degradation of hemicellulose starts at 150 °C and major weight loss occurs above 200 °C [18]. During the thermal degradation, hemicellulose generally gives off light volatiles producing less char and tars. It is partly depolymerized by the hydrolysis or thermal chain scission to provide reacting hemicellulose. This intermediate part is then decomposed and recombined to form thermally degraded hemicellulose. During thermal degradation, water and acids are produced and released into the surroundings [19].

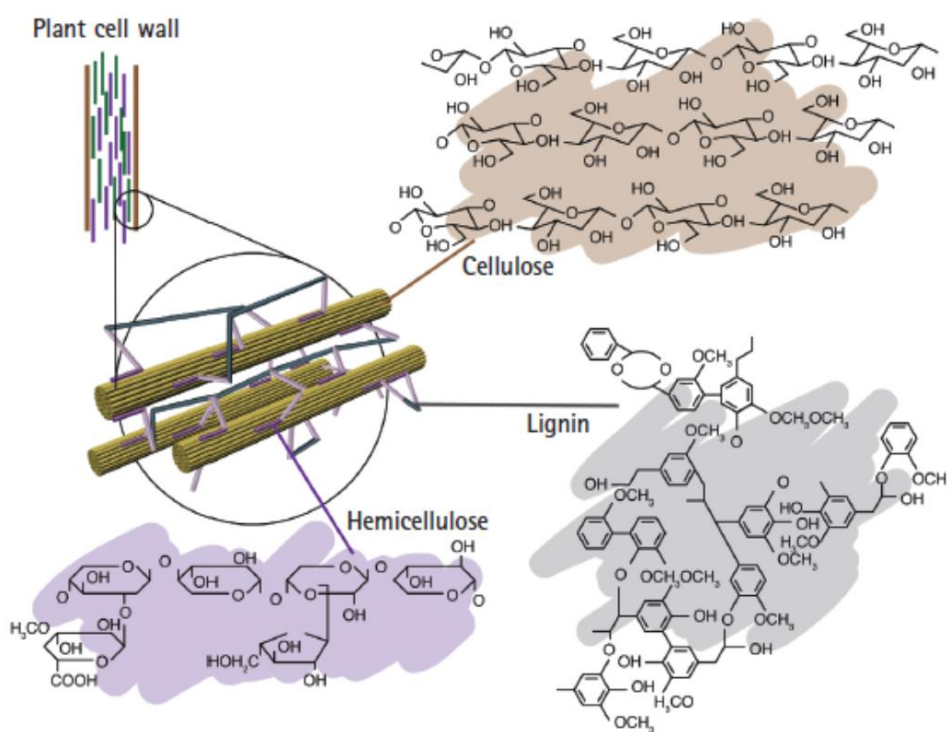


Figure 1.2: The composition of plant cell wall and biomass [14]

Cellulose, a polymer having 10^6 and higher molecular weight, is the fibrous part of wood and biomass [20]. Hydroxyl group in the glucose consists of hydrogen and oxygen present in the same chain as shown in Figure 1.2. All the monomers of glucose are meshed together in such a way that they form a carbohydrate matrix and provide stiffness to plant cells. The structure of cellulose is crystalline than hemicellulose that is why it resists to the thermal degradation. The amorphous part

of cellulose holds water of hydration which converts to vapors during thermal degradation and ruptures the structure. The cellulose decomposition occurs at 240 °C – 350 °C [21].

Lignin is a highly branched, amorphous, cross linked macromolecule and polyphenolic resin with no impeccable structure. Figure 1.2 shows a typical example of lignin polymer. Lignin fills the gaps between cellulose, hemicellulose and pectin components of plant cell wall. It acts as glue, thus cementing the plant cell structure. It is hydrophobic in nature. The thermal decomposition of lignin starts in the temperature range of 280 – 500 °C producing phenols [22]. It is very hard for lignin to dehydrate and is converted to char more than hemicellulose and cellulose.

The utilization of biomass as energy carrier has gradually increased in both developing and developed countries in last two decades. In 2009, Brazil spent \$ 7.8 billion in RE while in Sweden the share of biomass in energy surpassed that of oil [23]. However, biomass has certain issues which are big barriers for its use as an alternative solid fuel at commercial scale. The inherent properties of biomass like high moisture content and slagging makes it an inefficient fuel at larger scale. Slagging is the deposition of the mineral matter on the heat transfer surfaces. It makes an insulative layer which reduces the heat transfer efficiency [24]. The slag softens at the combustion temperature and sticks to the heat surfaces which causes an inhomogeneous distribution of the combustion air. The unburned fuel particles can trap in the slag as a result the carbon content of slag increases. Due to the capturing of particles, the chemical energy of unburned carbon is lost thus reducing the overall heat transfer efficiency of the boiler. The molten slag can also erode the boiler tubes and refractory lining [25,26]. When molten ash moves upward in the heat exchanger (by updrafts), it collides with the walls and tubes of the equipment and forms an insulative layer which reduces the heat transfer from the flue gas to water and steam. The flue gas will have the

higher enthalpy and temperature when leaving the heat exchanger and the caloric efficiency of equipment decreases [24].

The high moisture content, due to hydrophilic nature in raw biomass, decreases the efficiency of the thermal processes such as combustion, gasification and carbonization, and increases the cost. It also leads to low energy density, natural decomposition (fungal attack and biodegradation) and uncertainty in physical, chemical and microbiological properties. The higher oxygen content in the raw biomass as compared to hydrogen and carbon contents makes it less efficient for thermochemical conversion processes [15]. Due to high moisture content and slagging, higher amounts of raw biomass are needed than fossil fuel to produce the same amount of energy [23].

To address the above described challenges and make biomass a suitable energy source for the power generation, it has to be pretreated. The effects of pretreatment on the biomass is presented in Figure 1.3.

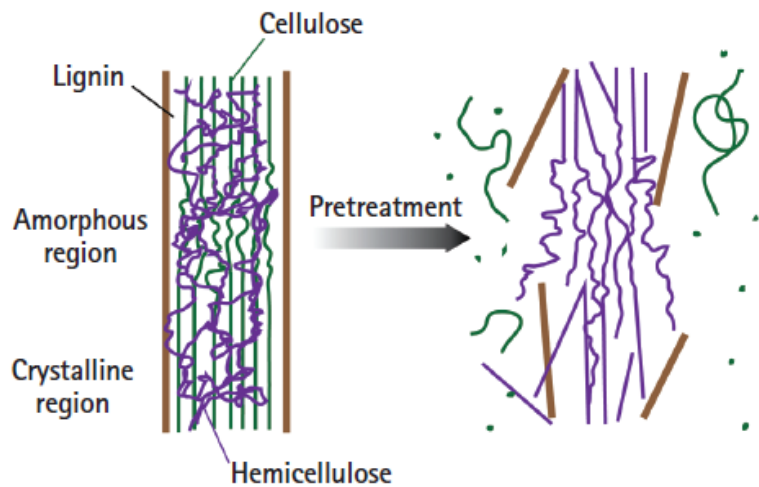


Figure 1.3: The effect of pretreatment on biomass [14]

The pretreatment of biomass converts it into useful form and helps in enhancing the physical properties such as grindability, improved shelf life and hydrophobic behavior, and chemical

compositions of the biomass thus making it an efficient solid fuel. The pretreatment process may be a thermal, chemical or mechanical process.

Depending on the final product, number of processes are available for the pretreatment and conversion of biomass as shown in Figure 1.4 [23]. The biochemical processes are time consuming while mechanical processes require a lot of input energy. Among various thermochemical processes, pyrolysis and carbonization take place at high temperature ($> 400\text{ }^{\circ}\text{C}$) while palletization requires high amount of input energy and addition of a binder reduces the calorific value of the biomass [27]. Although, drying of the biomass occurs at a lower temperature ($100\text{ }^{\circ}\text{C}$) but it does not improve the hydrophobic nature of the biomass [28]. Torrefaction, a thermal pretreatment process, is the thermolysis of lignocellulosic material in the temperature range of $200 - 300\text{ }^{\circ}\text{C}$.

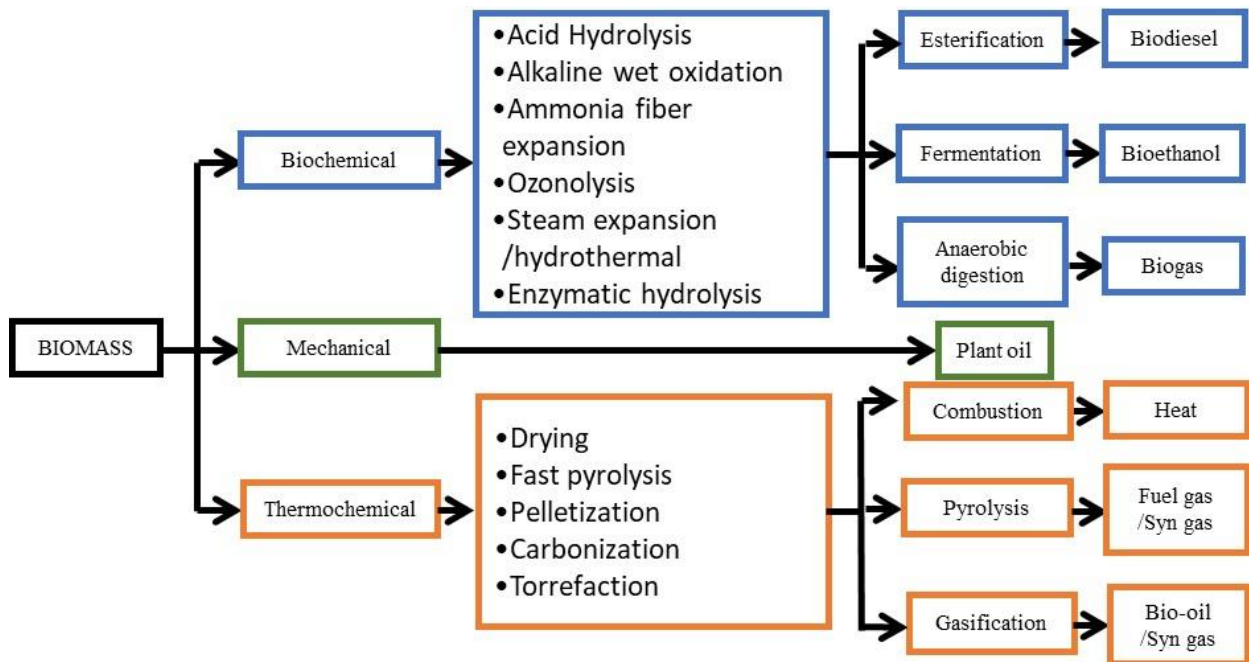


Figure 1.4: Summary of biomass pretreatment and conversion routes [22]

The torrefaction process is carried out at an atmospheric pressure and in inert environment [15,29]. Torrefaction process has a promising effect on the biomass as it converts raw biomass to an efficient and suitable solid fuel for the commercial and residential utilization. The effect of temperature, biomass decomposition reactions and different physio-chemical changes during torrefaction process is shown in Figure 1.5. The parameters which play an important role in the torrefaction process are (1) reaction temperature, (2) absence of oxygen, (3) pressure, (4) feedstock moisture, (5) residence time, (6) heating rate, (7) feedstock type and (8) feedstock particle size [30].

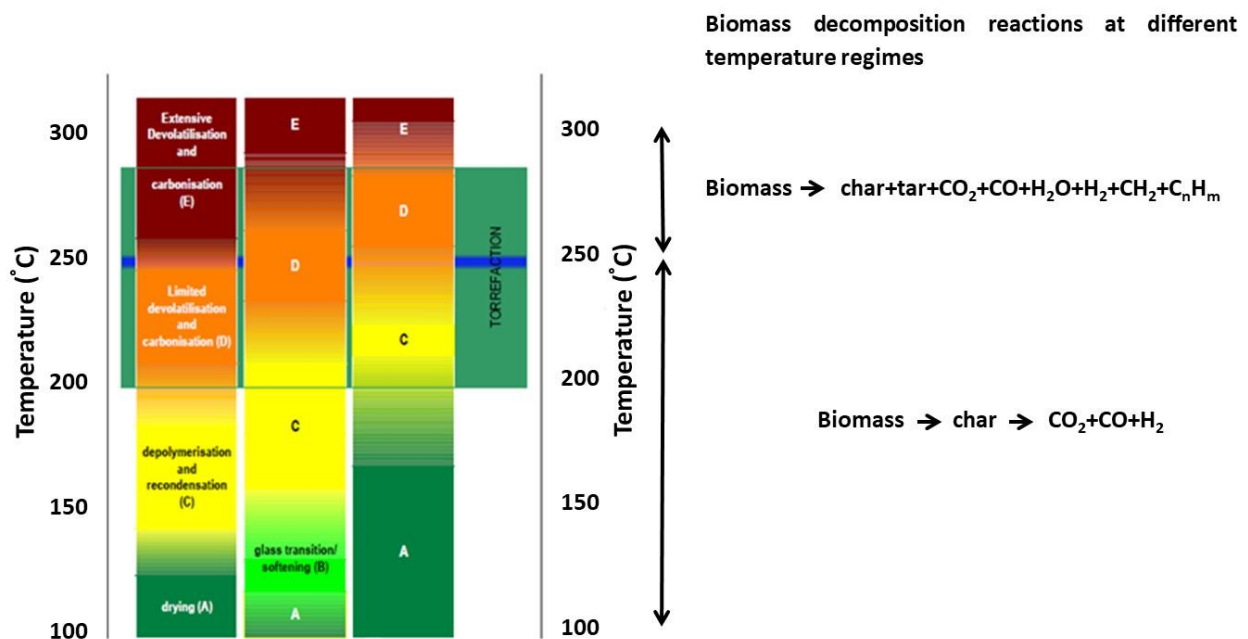


Figure 1.5: The effect of temperature on biomass during torrefaction process [31,32]

The torrefaction process causes the hemicellulose to decompose. Cellulose and lignin are also decomposed in the temperature range of 200 - 300 °C but the degree of decomposition is less than that of hemicellulose. With the rise in the temperature, the decomposition of cellulose and lignin

becomes significant [31]. The prominent reactions taking place during the torrefaction process are tabulated in Table 1.2. The severe drying in the torrefaction process causes the cell wall and tissues of biomass to collapse as the water and some of the volatile material are being removed thus instigating the shrinkage of biomass [32]. There are three mechanisms which result in the structural change of biomass during thermal treatment. Firstly, the high temperature starts thermal degradation of different components of biomass. Secondly, as water is removed, the pore wall starts to collapse and results in closure of pore wall due to the irreversible hydrogen bonding. Thirdly, the anisotropic drying shrinkage of cell wall layers [33–37].

Table 1.2: Reactions taking place during the torrefaction process at different temperatures [14]

Temperature (°C)	Time (min)	Process reactions
50 - 150	30-120	Nonreactive drying (moisture removal and structural changes)
150 - 200	30-120	Reactive drying (moisture removal and structural damage due to cell wall collapse)
200 - 300	<30	Destructive drying <ul style="list-style-type: none"> • Devolatilization and carbonization of hemicellulose • Depolymerization and softening of lignin • Depolymerization and devolatilization of cellulose

An overview of torrefaction products is shown in Figure 1.6. In torrefaction process, three products are formed: (1) solid biomass having brown-black color, (2) volatile organic compounds (condensable) like water, aldehydes, ketones, acetic acid and alcohols, and (3) gases (non-condensable) like CO, CO₂ and minor amounts of CH₄ [38]. The release of non-condensable and condensable compounds changes the chemical, physical and storage properties of biomass.

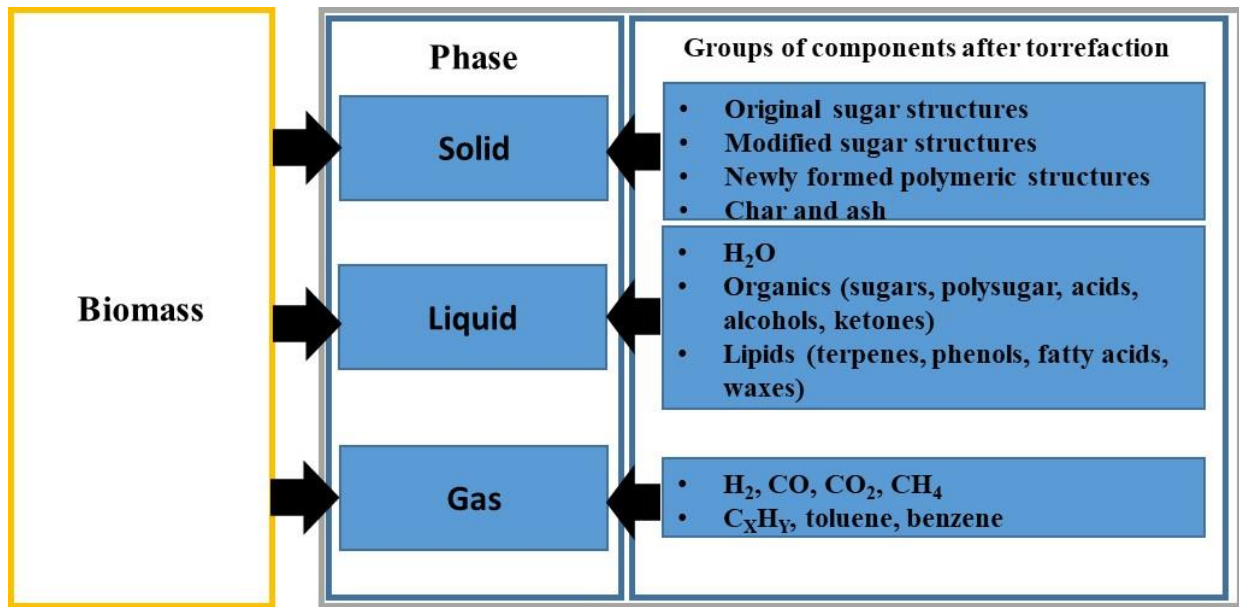


Figure 1.6: An overview of products formed during the torrefaction of biomass [40]

1.2 Project scope

Currently, the major existing large-scale firing systems are pulverized fuel system and have the potential to use biomass as a fuel. Although, the torrefaction process makes biomass compactable, hydrophobic, grindable, lowers its oxygen to carbon ratio (O/C) and increases its energy density, however, it does not tackle the slagging problem. The slagging problem of biomass can be addressed by the demineralization process. In the demineralization process, leaching agents (dilute solutions of strong acids) are used. The leaching agents dissolve the alkali and alkaline earth metals (AAEM) from the biomass and help in reducing its slagging issue.

Pakistan has rich resources of the agricultural residues and is not utilizing them in power generation. The biomass can be used to develop an economically feasible, environmentally acceptable and efficient solid fuel to address the energy shortfall [28,39–43]. The present study is aimed to treat the biomass with the suitable leaching agent and then thermolyzed it through the torrefaction process. The pretreatment processes adopted in this research are intended to improve

the fuel characteristics of biomass as well as its shelf life. The success of this investigation will direct us to utilize the upgraded biomass for the power generation at commercial scale.

1.3 Research objectives

In this research work, the aim is to enhance the energy value and fuel characteristics of the biomass by the application of the combine process. To achieve this, the following are the research objectives;

- To study the effect of different leaching agents and leaching time on the biomass during the demineralization process
- To investigate the influence of temperature and residence time on the biomass during the torrefaction process
- To determine the thermal degradation profiles of demineralized and torrefied biomass
- To investigate the effect of torrefaction on the energy and mass yield (%), calorific value and hydrophilic nature of biomass
- To evaluate the impact of the torrefaction on the fuel characteristics of demineralized biomass

1.4 Structure of thesis

The thesis comprises of six chapters and chapter 3, 4 and 5 is written in the manuscript format.

Chapter 2 will cover the literature related to the application of torrefaction and demineralization on the composition, calorific value and hydrophilic nature of the biomass. In **Chapter 3**, the effect of demineralization on the physio-chemical structure and thermal degradation of biomass by different leaching agents will be discussed. The dilute (5 wt. %) solutions of HCl and H₂SO₄ were used for the demineralization of rice husk separately with leaching time of 15, 60 and 120 min. It is observed that H₂SO₄ exhibited higher removal of AAEM comparatively as depicted by the 34.20% decrease in ash content along with an increase of 7.10% in the heating value. At the same instant, H₂SO₄ has been seen to induce more notable changes in physiochemical structure as depicted by the fourier transform infrared (FTIR) spectra and scanning electron microscopy (SEM)

micrographs. A slight change in intensity of bands around 1730 cm^{-1} and 1650 cm^{-1} of rice husk treated with both acids for 120 min can be observed which is probably due to the high removal of inorganics comparatively. The shifting of peaks of treated samples towards high temperature in thermogravimetric (TG) and derivative thermogravimetric (DTG) curves showed that treated sample are more resistant towards thermal degradation due to the elimination of catalytic role of AAEM. **Chapter 4** illustrates the effect of torrefaction, performed at different temperatures and residence time, on the thermal degradation and physio-chemical structure of biomass. For this, torrefaction of biomass at three different temperatures 200, 250, and $300\text{ }^{\circ}\text{C}$ for four different residence time 10, 30, 90 and 150 min has been performed. The torrefied biomass has been found to be approaching the characteristics of the coal. An overall increase in the higher heating value (HHV) and decrease in the energy and mass yield was observed with the increase in residence time and temperature. FTIR spectrum showed a clear decrease in O–H peak intensity thus hydrophobic nature of biomass was improved. TGA and DTG curves demonstrated decrease in hemicellulose content because of its dehydroxylation which is also evident from the SEM micrographs. The effects of torrefaction on the demineralized biomass are presented in **Chapter 5**. For assessment of compositional changes, X-ray Fluorescence (XRF), ultimate and proximate analysis were performed. The XRF analysis confirms the removal of AAEM thus reducing the slagging nature of treated samples. The pretreatment processes upgrade the carbon content from 32.45 - 43.10%, hence also improved the HHV from 3939 - 4356 cal.g^{-1} . The reduction in the oxygen and hydrogen content is observed from 45.92 to 36.08% and from 5.44 to 4.30%, respectively which improves the hydrophobic behavior as water uptake of the treated samples reduces by 55 %. **Chapter 6** presents the conclusion of research work and future recommendations.

CHAPTER 2: LITERATURE REVIEW

The biomass is produced from photosynthesis of the plant. The plant captures the solar energy and consumes it to convert water (H_2O) and carbon dioxide (CO_2) into glucose ($C_6H_{12}O_6$) which acts as a food in plant growth during photosynthesis. As the energy stored in the plant is from the sun, that is why biomass is categorized as a RE source [44]. The energy can be produced from biomass by direct and indirect routes. In the direct route, electricity is generated by direct combustion of biomass feed stock [45]. While the indirect route derives energy from the biomass in the form of energy products such as gasification is used to form the producer gas [46], fermentation converts the biomass in ethanol [47] and pyrolysis produces the liquid fuels [48]. However, the slagging problem of the biomass puts a big barrier on its use in the combustion and pyrolysis processes [49,50] while the gasification of the biomass has created a very little impact due to its high capital cost [51]. The ethanol production from the agricultural residues has the disadvantages of low reaction speed and yield [52].

The abundant availability and renewable nature make the biomass a very promising alternative fuel. However, the inherent issues of the biomass create problems for energy generation at commercial scale. One of the major problem of the biomass is its affinity towards moisture due to its hygroscopic nature. The moisture content affects the bulk density of the biomass, increases its transportation cost and reduces the efficiency of the combustion process [53,54]. As compared to fossil fuel, biomass has high oxygen content as well. The oxygen content in the coal varies from 8 – 24% by weight [55,56] while the oxygen content values of the biomass are from 30 – 45% (by weight) [57]. The higher oxygen content in biomass lowers its calorific value and high amount of biomass is needed to generate the same energy output as fossil fuel [58]. Another major problem of the biomass is its slagging nature due to which molten mineral matter deposits on the walls and

heat transfer surface of a heat exchanger [59] as shown in Figure 2.1. In heat exchangers (boiler and furnace), slagging takes place in the high temperature regions. The mineral matters are carried by the ash content of the biomass and the major elements in the ash are Si, K, Mg, Al, Na, Fe, Ca and P. Some minor elements (Cr, Co, Cd, Cu, Mo, Pb and Ni) are also present [60]. The presence of major mineral matters (alkali and alkaline earth metals, AAEM) lower the melting point of the ash and increases the slagging [61]. The ash content has also an effect on calorific value of the biomass as it decreases the combustible compounds and heating potential of the biomass. The inorganic matter limits combustible compounds in the biomass and thus the heating potential of the biomass decreases.



Figure 2.1: Ash slagging in the heat exchangers

Trischler et al. reported that when ash content in the biomass increases from 0.10 - 6.80%, the calorific value of the biomass decreases from 3.32 - 0.90 MWH/m³. To address the above described issues, the biomass has to be pretreated. Torrefaction process, a thermal treatment of the biomass in the temperature range of 200 – 300 °C under inert environment, tackles the issue of hygroscopic nature of the biomass while the demineralization process, leaching of the biomass with the weak solutions of the strong acids, addresses the slagging nature of the biomass.

Pach et al. performed the torrefaction of birch, pine and bagasse in a cylindrical reactor at 230, 250 and 280 °C with 1, 2 and 3 hr residence time. The solid yield ranged 68.90 – 86.90% for birch, 67.10 – 92.40% for pine and 63.80 – 87.50% for bagasse. The release of the volatile matter increased the ash content of thermally treated biomasses [62]. The similar effect of residence time and temperature have been reported by Pentananunt et al. [63]. With the loss of the mass, OH group is reduced which reduces the moisture adsorption capability of the torrefied biomasses [64,65]. The torrefaction of the logging residues and pine chips at temperature 225 – 300 °C for 30 min was studied. The calorific values of logging residues and pine chips increased by 41% and 37% respectively [66]. Prins et al. found the 17% and 20% increase in the energy content of willow when torrefied at 270 and 280 °C respectively [67].

The effect of demineralization, using hydrofluoric acid (HF), hydrochloric acid (HCl), distilled water and tap water as leaching agents, on poplar wood powder were studied. The TGA revealed that the degradation temperature of the leached biomass increased slightly from 362 °C to 372, 366 and 368 °C [42]. The same trend of rise in the thermal degradation temperature was observed by Asadieraghi et al. [41]. Eom et al. investigated the effect of potassium (K), calcium (Ca) and magnesium (Mg) on thermal decomposition of the biomass. The TGA showed that the biomass degradation temperature and the char formation were affected by K, whereas the degradation rate was influenced by the Mg and Ca [40]. The impact of diverse leaching methods on the AAEM removal, the combustion characteristics and ash behavior were studied. It was reported that the AAEM removed by leaching have catalytic effect on char combustion and volatiles evolution [68].

The following sections will explain the effect induced by the demineralization and torrefaction on the composition and energy potential of various biomasses.

2.1 Ultimate and proximate analysis

The ultimate analysis of biomass is an important technique as it shows the exact amount of atomic elements in a sample by weight. The elemental composition in the biomass can vary depending on the region from which the biomass is taken and biomass type. The major four elements in a biomass are carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) [57,69]. The higher amount of the carbon content in the biomass increases its energy potential/calorific value while the high oxygen content in the biomass is not favorable as this enhances the moisture adsorption capability of the biomass [70]. The ultimate analysis data of different biomasses treated at different torrefaction conditions have been tabulated in Table 2.1. The torrefaction process emanated in increased carbon content of the biomass while its oxygen and hydrogen contents showed a declining trend. That is why torrefied biomass has an enhanced energy value than the raw biomass.

Table 2.1: Ultimate analysis of different biomass under different torrefaction process conditions

Biomass	Time (hr)	Temperature (°C)	C (wt. %)	H (wt. %)	N (wt. %)	O (wt. %)	Ref.
Coffee residue	0.5	240	50.83	6.66	2.74	37.75	[71]
	0.5	270	55.93	5.60	2.67	32.52	
	1	240	52.10	6.36	2.57	36.43	
	1	270	65.10	5.52	2.94	22.50	
Saw dust	0.5	240	42.49	5.34	2.80	33.08	
	0.5	270	43.48	4.78	3.14	30.12	
	1	240	43.46	5.25	2.93	31.57	
	1	270	48.67	4.79	3.18	22.99	
Rice husk	0.5	240	44.19	5.35	0.10	37.81	
	0.5	270	46.59	5.15	0.09	33.76	
	1	240	44.28	5.32	0.09	37.46	
	1	270	48.15	4.75	0.11	31.26	
Reed canary grass	0.5	250	50.30	6.30	0.00	37.00	[72]
	0.5	270	54.30	6.10	0.10	36.30	
Wheat straw	0.5	250	49.60	6.10	0.90	35.60	
	0.5	270	56.40	5.60	1.00	27.60	
Willow	0.5	250	51.70	6.10	0.20	38.70	
	0.5	270	54.70	6.00	0.10	36.40	
Eucalyptus	0.5	270	57.80	6.00	0.00	36.20	[73]

	1	270	61.90	5.80	0.00	32.30	
Yellow poplar	0.5	240	49.47	5.93	0.13	31.38	[29]
	0.5	260	51.60	5.83	0.14	28.73	
	0.5	280	54.03	5.65	0.14	28.06	
Bamboo	1	220	49.60	5.96	0.26	44.18	[74]
	1	250	53.47	5.59	0.31	40.63	
	1	280	58.43	5.10	0.34	36.13	
Corn stover	0.5	200	45.80	5.50	0.60	48.10	[75]
	0.5	250	48.80	5.20	0.90	45.10	
	0.5	300	59.0	4.70	1.00	35.40	
Bagasse	1	230	48.60	5.60	0.25	45.50	[62]
	1	250	50.60	5.60	0.30	43.50	
	1	280	52.80	5.30	0.39	41.50	
Kernel shell	1	220	45.87	6.31	0.40	43.07	[39]
	1	250	51.89	5.71	0.47	38.50	
	1	300	54.21	5.08	0.50	36.66	
Empty fruit bunches	1	220	46.75	4.68	1.27	41.42	[39]
	1	250	47.07	4.95	1.35	42.24	
	1	300	49.56	4.38	1.27	43.19	

Van Krevelen diagram, Figure 2.2, shows that the raw biomass has higher atomic hydrogen to atomic carbon ratio (H/C) and atomic oxygen to atomic carbon ratio (O/C) in comparison to other solid fuels such as anthracite, coal, charcoal, lignite and peat.

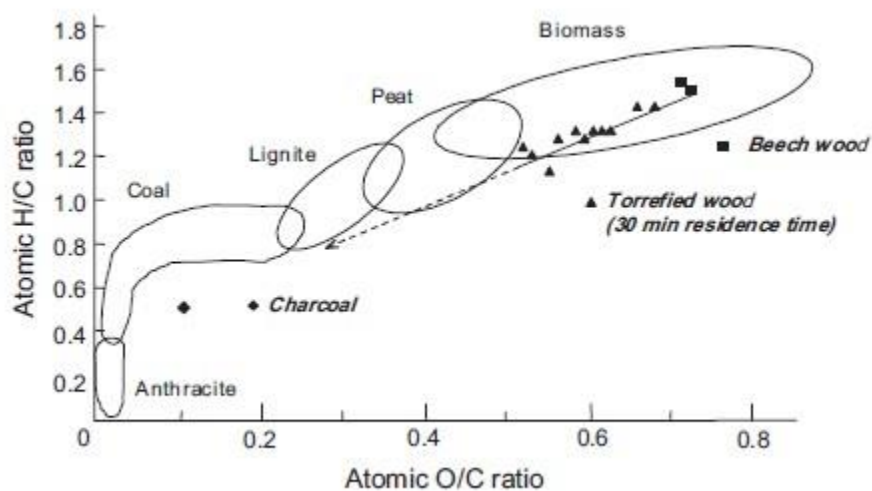


Figure 2.2: Van Krevelen diagram [15]

At intense torrefaction process conditions, the biomass position in Van Krevelen diagram improves and approaches towards coal as the removal of volatile matter and oxygen is more compare to the torrefaction carried out at low temperature and residence time [76].

The proximate analysis determines the weight percentages of fixed carbon (FC), ash content, volatile matter (VM), and moisture in the material. The ash content of a sample is the incombustible and inorganic part which remained after the sample has been completely oxidized. Although the coal has high ash content but the composition of coal ash and biomass ash are different. Since the equipment are designed for the coal, the biomass ash creates major issues in them. The biomass ash is rich in AAEM and is highly reactive. During the combustion process, the biomass ash causes the slagging and corrosion [55]. The VM in the biomass is high when compared to fossil fuel (coal), which is its main drawback as the high VM mean high oxygen content which reduces the calorific value of the biomass [77]. The data of proximate analysis of biomasses torrefied at different processing conditions is presented in Table 2.2. The tabulated data shows that torrefaction process has resulted in increased FC content while the VM content has reduced. The change in proximate analysis of the torrefied biomass is due to the removal of the oxygen and hydrogen in the form of VM when compared to the raw biomass. The mineral matter present in the biomass plays a catalytic role in the removal of VM [28,78]. The ash content, present inherently in the biomass feedstock, has a relative impact on torrefaction product and it generally increases from 0.10 - 12 % during torrefaction in comparison to FC content which changes from 0.90 - 29% [72,79,80].

Table 2.2: Proximate analysis (dry basis) of different biomass under different torrefaction process conditions

Biomass	Time (hr)	Temperature (°C)	VM (wt. %)	FC (wt. %)	Ash (wt. %)	Ref.
Pine chips	0.5	225	84.78	14.95	0.27	[66]
	0.5	250	82.52	17.24	0.25	
	0.5	275	76.40	23.26	0.35	
	0.5	300	58.72	40.85	0.43	
Reed canary grass	0.5	250	80.30	13.30	6.40	[72]
	0.5	270	76.60	16.10	7.30	
	0.5	290	70.50	21.30	8.30	
Wheat straw	0.5	250	77.00	15.60	7.40	[72]
	0.5	270	65.20	26.50	8.40	
	0.5	290	51.80	38/00	10.20	
Willow	0.5	250	79.80	18.40	1.90	[72]
	0.5	270	79.30	18.60	2.10	
	0.5	290	77.20	20.50	2.30	
Bamboo	1	220	75.20	22.48	2.32	[74]
	1	250	67.93	29.19	2.88	
	1	280	58.80	37.78	3.42	
Bagasse	1	250	65.49	26.82	2.89	[79]
	1	270	60.03	32.97	2.91	
	1	300	40.44	51.63	4.12	
Cotton stalk	0.5	200	44.43	41.89	8.44	[35]
	0.5	250	36.13	44.48	12.69	
	0.5	300	31.16	48.00	14.74	
Rice husk	1	250	54.76	19.73	21.56	[79]
	1	270	49.99	21.75	24.57	
	1	300	30.04	35.97	31.32	
Peanut husk	1	250	50.86	20.05	24.48	[79]
	1	270	45.47	23.81	26.84	
	1	300	38.82	23.86	33.77	

2.2 Calorific value

The calorific value of a fuel is determined by taking the ratio of the heat of reaction of complete combustion to the mass of the sample [81]. It is one of the key characteristic for a biomass residue.

The calorific value can be defined in two ways, higher heating value (HHV) and lower heating value (LHV). The difference between the HHV and LHV is that HHV includes latent heat of

vaporization of water while LHV does not include it [82]. The HHV of different biomasses torrefied under different process conditions are listed in Table 2.3. During the torrefaction process, the HHV of the biomass increases as its carbon content increases and oxygen content decreases [76]. The net calorific value of the torrefied biomass is 18 - 23 MJkg⁻¹ (LHV, dry basis) or 20 - 24 MJkg⁻¹ (HHV, dry basis) [83,84] and this energy is stored in the biomass for quite a long time as its shelf life is also enhanced by the torrefaction process.

Table 2.3: HHV of different biomasses torrefied under different process conditions

Biomass	Time (hr)	Temperature (°C)	HHV (kJkg⁻¹)	Ref.
Reen canary grass	0.5	250	20,000	[72]
	0.5	270	20,800	
	0.5	290	21,800	
Wheat straw	0.5	250	19,800	[72]
	0.5	270	20,700	
	0.5	290	22,600	
Willow	0.5	250	20,600	[72]
	0.5	270	21,400	
	0.5	290	21,900	
Pine chips	0.5	225	19,480	[66]
	0.5	250	20,080	
	0.5	275	21,820	
	0.5	300	25,380	
Bamboo	1	220	19,300	[74]
	1	250	21,000	
	1	280	23,100	
Eucalyptus	0.5	270	22,800	[73]
	0.5	290	27,300	
Miscanthus	1	230-250	21,100	[85]
	0.5	290	25,200	
Corn stover	0.5	200	18,400	[75]
	0.5	300	21,600	
Rice straw	0.5	200	17,160	[43]
	0.5	250	18,030	
	0.5	300	18,680	
Rape stalk	0.5	200	19,500	[43]
	0.5	250	20,100	
	0.5	300	21,590	
Bagasse	1	230	17,080	[62]

	1	250	18,080	
	1	280	18,730	
Cotton stalk	0.5	200	23,940	[35]
	0.5	250	24,570	
	0.5	300	25,030	
Peanut husk	1	250	16,350	[79]
	1	270	18,600	
	1	300	18,960	
Sawdust	1	250	19,550	[79]
	1	270	20,470	
	1	300	23,800	

2.3 Energy yield (EY) and mass yield (MY)

The EY and MY describes the chemical energy and transition of mass to the solid product from the raw biomass. Table 2.4 shows a typical energy and mass distributions of a biomass, willow. At the applied process conditions, the major amount of energy is stored in solid product and the energy value of the VM is majorly stored by organics and lipids.

Table 2.4: Energy and mass distribution of willow at 280 °C for 17.5 min reaction time [54]

Reaction products	MY (%)	EY (daf) (%)
Solid	87.5	94.9
Lipids	1.4	3.4
Organics	1.7	1.6
Gases	1.4	0.1
Water	8.0	0.0

Note: (daf: dry and ash-free basis)

The biomass properties and torrefaction process conditions have a pronounced effect on the amount of torrefaction products as shown in Table 2.5 [15,86]. The straw has the higher amounts of liquid and gas products, larch has the lowest while willow is in between straw and woody biomass. With the increase of temperature and time, the volatile production increases and solid

char production decreases because at intense processing conditions, devolatilization reactions are pronounced.

Table 2.5: Overall mass balance of several torrefaction experiments [14,57]

Biomass	Time (min)	Temperature (°C)	Product Yield (wt. %)		
			Gaseous	Liquid	Solid
Willow	50	230	3	4	93
	100	230	2	7	91
	30	250	4	4	88
	60	250	3	11	84
	15	270	3	14	82
	30	270	3	12	80
Larch	50	230	-	2	98
	30	250	1	2	97
	15	270	1	4	91
Straw	30	250	2	10	85

Table 2.6 shows the torrefaction effect on the MY and EY of various biomass residues for different torrefaction residence time and temperature. Although, with increase in process temperature and residence time, the mass and energy yield decreases but HHV of the torrefied biomass increases as torrefaction reduces oxygen which raises the energy potential of the biomass.

Table 2.6: Effect of torrefaction process conditions on the MY and EY of various biomass residues

Biomass	Time (hr)	Temperature (°C)	MY (wt. %)	EY (wt. %)	Ref
Yellow poplar chips	0.5	240	94.00	99.90	[29]
	0.5	260	81.90	91.40	
	0.5	280	68.50	80.40	
Pine chips	0.5	225	89.00	94.00	[66]
	0.5	250	82.00	90.00	
	0.5	275	73.00	87.00	
	0.5	300	52.00	71.00	
Willo	0.17	290	81.60	89.90	[85]

miscanthus	0.17	290	75.70	81.00	
eucalyptus	0.5	270	67.62	74.00	[73]
	1	270	56.66	67.50	
	0.5	290	50.61	67.70	
Wheat	0.5	230	91.00	93.50	[72]
straw					
	0.5	250	82.60	86.20	
	0.5	270	71.50	78.20	
	0.5	290	55.10	65.80	
Canary	0.5	250	84.00	86.60	
grass					
	0.5	270	72.00	77.10	
	0.5	290	61.50	69.00	
Coffee	0.5	240	89.50	95.50	[71]
	0.5	270	74.00	92.00	
	1	240	84.00	94.00	
	1	270	64.00	88.50	
Saw dust	0.5	240	92.50	98.50	
	0.5	270	82.00	93.50	
	1	240	88.00	97.00	
	1	270	77.00	87.50	
Bagasse	1	230	87.50	96.42	[62]
	1	250	78.90	92.03	
	1	280	68.60	82.90	
Corn stover	0.33	250	86.20	89.00	[75]
	0.5	200	98.40	≈100	
Cotton stalk	0.5	200	63.89	83.44	[35]
	0.5	250	33.80	45.30	
	0.5	300	30.04	30.04	
Peanut husk	1	250	72.50	81.02	[79]
	1	270	67.00	85.18	
	1	300	55.75	72.25	
Rape stalk	0.5	200	63.29	65.82	[43]
	0.5	250	38.26	41.01	
	0.5	300	25.30	29.13	
Rice straw	0.5	200	59.84	59.98	[43]
	0.5	250	40.32	42.46	
	0.5	300	36.57	39.90	

2.4 Effect of demineralization on removal of mineral matter

The slagging problem of biomass can be addressed by the demineralization of biomass using leaching agents. Jiang et al. compared the efficiency of different leaching agents (5 wt. %

solutions) which were mixed at 10 ml.g⁻¹ ratio with the biomass residue. The specimen was stirred for two hours at room temperature. The acid treated biomass was then washed with deionized water until neutral pH was attained. The results are tabulated in Table 2.7 and showed that leaching is effective in reducing the ash and the mineral components of biomass [87]. The demineralization process also has some adverse effects on the biomass as leaching agents disturbs the organic part of the biomass. It was reported that the surface porosity of the biomass was increased after the treatment as some particles were leached away [41]. The epidermis and stomata of biomasses were changed which could be an evidence that the acid solutions change the fiber structure by hydrolyzing cellulose and hemicellulose.

Table 2.7: Demineralization of rice straw [87]

Sample	Demineralization efficiency				
	K	Ca	Fe	Na	Mg
DI-H ₂ O-RS	82.3	17.1	56.6	80.4	33.5
CH ₃ COOH-RS	99.4	21.8	54.2	81.6	91.3
HCl-RS	99.7	97.9	76.3	88.1	99.2
H ₂ SO ₄ -RS	99.8	95.7	68.5	88.5	98.6
HNO ₃ -RS	99.7	96.8	65.0	84.8	99.1
H ₃ PO ₄ -RS	99.7	62.3	57.9	86.2	98.7

The biomass residues can be used as a solid fuel in the power generation, however the hygroscopic nature of the biomass reduces its energy potential and shelf life while the slagging nature decreases the heat transfer rate in the heat exchange equipment and puts a threat on the safe operation of different heat exchanger such as boiler and furnace. The focus of the present research work is to develop a strategy that can address both inherent issues of the biomass.

CHAPTER 3: EFFECT OF DEMINERALIZATION ON THE PHYSIOCHEMICAL STRUCTURE AND THERMAL DEGRADATION OF ACID TREATED INDIGENOUS BIOMASS

3.1 Introduction

The current challenge to the world is to reduce its dependence on fossil fuel by developing sustainable and renewable energy supplies, due to the depletion of the fossil fuel reserves with increase in their price, and their use result in greenhouse effect and environmental pollution. Energy from biomass accounts for the largest renewable energy in the world [88]. Biomass is a lignocellulosic material mainly consisting of cellulose, hemicellulose, lignin, ash and extractives [42]. One important feature of biomass is that it contains alkali and alkaline earth metals (AAEM) such as potassium, sodium, magnesium, calcium, iron etc. [89]. AAEM are the main inorganic content of biomass. They are generally present less than 1% and may go up to 15% depending on the biomass type [90]. Higher AAEM content in biomass leads to slagging and fouling of the heat exchanger in the high temperature conversion systems. Slagging and fouling is the deposition of ash on the heat transfer surface forming an insulating layer which reduces the heat transfer causing corrosion and erosion problems. This condition puts the threat on the safe operation of the thermal systems and increases the cost of operation and maintenance. The main contributors in slagging and fouling are potassium and sodium which lower the melting point of ash resulting in ash deposition on heat transfer surface [91–93].

Demineralization of biomass has demonstrated to be an effective process for reducing the slagging and fouling nature of it by reducing AAEM content and improving its fuel properties for high temperature processes. Leaching agents (water and different acids) are used to demineralize the biomass in different studies [42,68,94–96]. Jiang et al. used deionized water, acetic acid, hydrochloric acid, sulphuric acid, nitric acid and orthophosphoric acid and found that sulphuric

acid and nitric acid were able to remove more AAEM than other leaching agents. Asadieraghi et al. demineralized palm oil biomass with sulphuric acid, hypochlorous acid, hydrofluoric acid, nitric acid and hydrochloric acid. Hydrofluoric acid removed more AAEM than other leaching agents. Although water has less adverse effect on the structure of biomass, however, it could hardly remove AAEM. High removal efficiency of AAEM was observed when acids were used, however, they had potential of attacking on acid soluble hydrocarbons present in biomass in the form of cellulose and hemicellulose. Therefore, it is necessary to evaluate the physiochemical and structural changes of biomass during demineralization [42,68,97,98], due to the negative impact of the acids.

The present chapter focuses on the changes on physiochemical structure of rice husk after demineralization using different leaching agents as well as its thermal degradation behavior.

3.2 Materials and Methods

3.2.1 Materials

Raw biomass, Rice Husk was supplied by a local rice mill located in Punjab, Pakistan. The raw material was firstly sieved by using a high vibratory sieve (Model 2Y1237, Sky Machinery) and mass fraction retained between 8 mm and 10 mm screen was selected for torrefaction process. The collected biomass was later washed with distilled water and dried in a rectangular shaped solar greenhouse dryer. The dryer was made up of steel frame with transparent polyethylene walls and roof. Ventilation holes were provided around all sides of the dryer for air circulation. The dried biomass was then stored in air tight bags before any further treatment.

3.2.2 Methods

3.2.2.1 Demineralization Process

The rice husk samples were cut into 2 mm particle size. The samples were placed in the dilute acid solutions keeping a solid to liquid weight ratio of 1:15. The mixtures of rice husk and leaching

agents were thoroughly mixed with the help of an orbital shaker at 200 rpm for three different leaching time intervals i.e. 15, 60 and 120 min at room temperature. The treated biomass samples were then washed with deionized water until the pH value approached to neutral. After washing, treated samples were dried in an oven at 60 °C for 24 hr and then were stored in the air tight bags for further analysis. The identification of each sample and actions performed on them are shown in Table 3.1.

Table 3.1: Identification and actions performed on each sample

Sr. No.	Sample Identification	Actions Performed	
		Leaching agent	Leaching time (min)
1	R	Raw Rice Husk	
2	R1	HCl	15
3	R2	-	60
4	R3	-	120
5	R4	H ₂ SO ₄	15
6	R5	-	60
7	R6	-	120

3.2.2.2 Scanning electron microscopy (SEM)

To examine the surface morphology of demineralized biomass, all samples were observed by the scanning electron microscopy (SEM (JEOL JSM-6490 LV) operating at low vacuum and 5 kV accelerating voltage. All the samples were spread on an adhesive carbon tape attached with a sample tab and sent into the SEM for scanning.

3.2.2.3 Fourier transform infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis was performed to study changes in the functional groups of biomass sample after demineralization using Cary 630 FTIR spectrometer, Agilent. Raw and acid treated biomass samples were individually grounded using a mortar and pestle. Each sample was placed directly on an Agilent diamond ATR sample interface. A sample

press was used to ensure that the samples were in good contact with the sensor surface. Spectral data was collected in the 4000–500 cm^{-1} region and analyzed using Agilent Microlab software.

3.2.2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves for raw and demineralized biomass samples were drawn by using a Thermogravimetric Analyzer SDT Q600 from TA Instruments. 10 mg of each sample was taken in a platinum crucible and placed in the furnace of SDT Q600 TA instrument. It was initially heated up to 105 °C in the presence of N_2 gas. The temperature was held constant at 105 °C for 5 min for moisture evaporation. Then temperature was raised to 500 °C in N_2 gas environment. To ensure complete combustion, the heating was continued for 10 min at 950 °C in the presence of O_2 . The heating rate for all cases was set at 10 °C/min.

3.2.2.5 Ash percentage and heating value

The ash percentage was calculated using ASTM 3174 where further details can be referred. The higher heating value (HHV) of raw and acid treated biomass samples was computed according to ASTM D-1989 by using an AC-500 isoperibol calorimeter from LECO. A mass of 0.2 g of each biomass sample was loaded in a glass crucible and placed inside the bomb. The bomb was filled with O_2 (99.5 %) and placed inside the water jacket. This assembly was then placed in AC-500 isoperibol calorimeter. After ignition by a pure cotton thread, the sample starts to combust and heat is released which is transferred to the water jacket causing the temperature of water to increase. The HHV of each sample was calculated based on the increase in temperature and expressed in MJ.kg^{-1} units.

3.1 Results and Discussion

3.3.1 Morphological features

Figure 3.1 shows the SEM micrographs of the raw and acid treated rice husk samples. The raw sample has clear structure where the plant epidermis and stomata are not damaged while fuzziness and erosion can be observed in the demineralized samples. The native sample has less porosity than the acid treated samples especially in case R5 and R6 which means H_2SO_4 as leaching agent has more significant effect on biomass structure by dissolving cellulose and hemicellulose [96,99]. Increased porosity also indicates that some material was leached away by dilute acid solutions. The removed particles from biomass might be extractives and minerals as observed in the literature [41]. The removal of minerals and extractives and dissolution of hemicellulose and cellulose may result in the higher availability of surface area and pore volume [100].

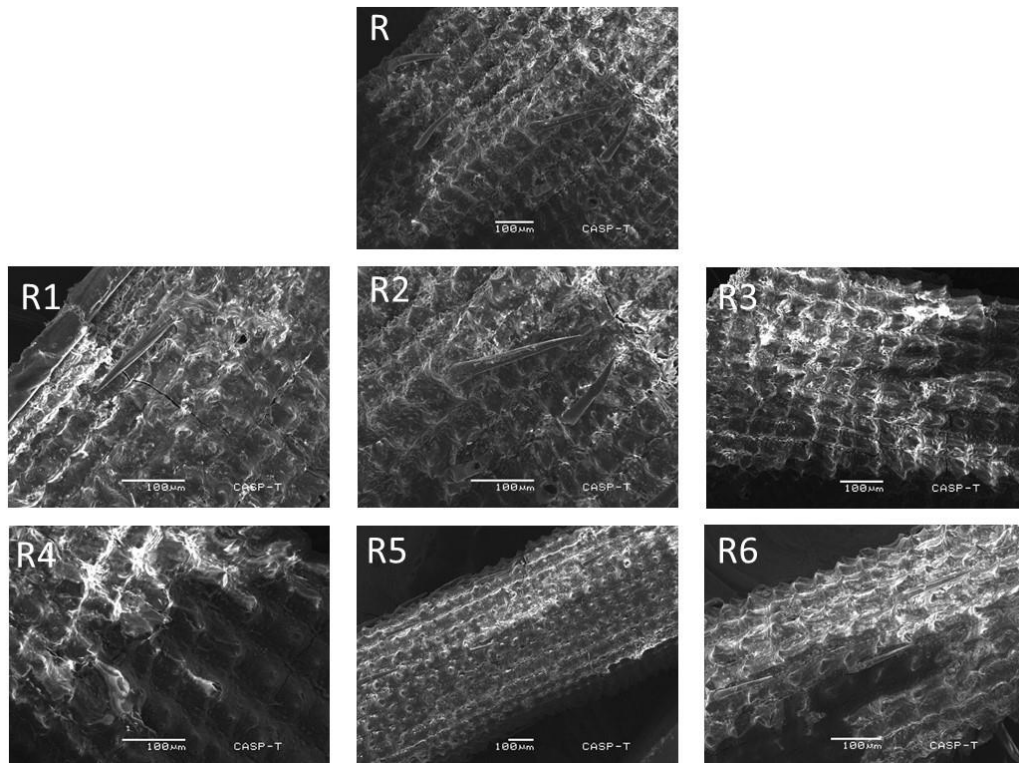


Figure 3.1: SEM micrographs of the raw and acid treated biomass samples

3.3.2 FTIR

The chemical structure evaluation of biomass is frequently studied using infrared spectroscopy. In this study, FTIR technique was used to investigate the impacts of acid treatment on the biomass chemical structure. Figure 3.2 and Figure 3.3 show the FTIR spectra of HCl and H₂SO₄ treated biomass samples respectively. In the spectra, the first broad band at 3700-3000 cm⁻¹ can be observed and it is related to O-H stretching vibrations of hydroxyl functional groups which may be present in phenolic, alcoholic and carboxylic structures.

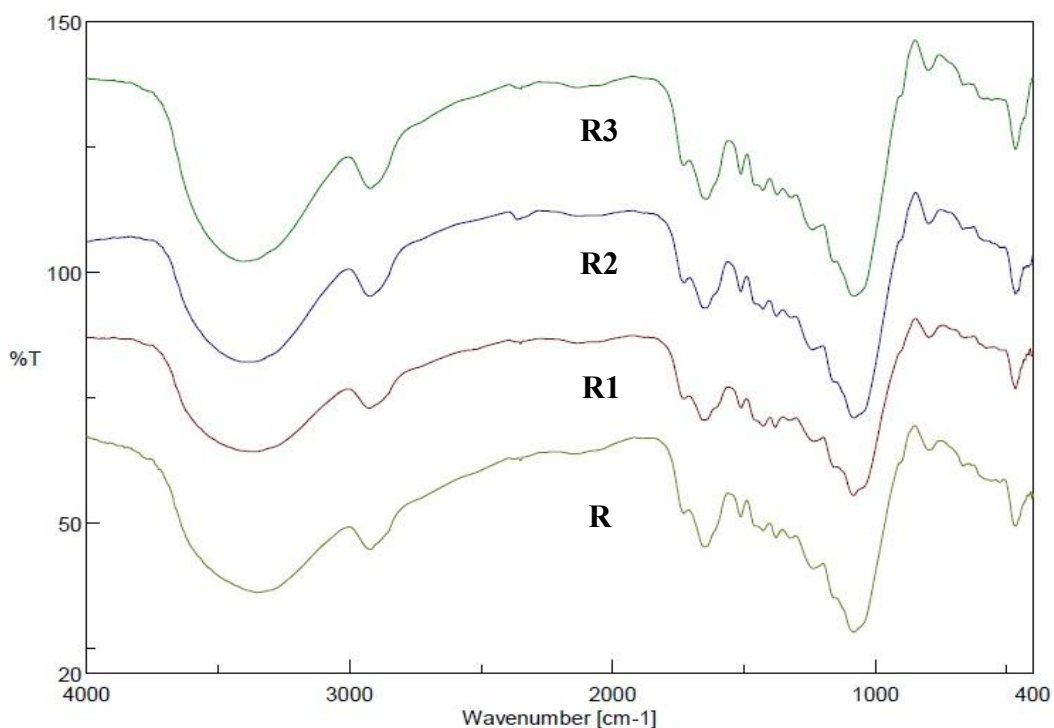


Figure 3.2: FTIR spectra of the raw and HCl treated samples

The band at 2800-3000 cm⁻¹ is attributed to C-H stretching vibration of -CH₂ and -CH₃ functional groups. A slight change in both bands can be observed after acid treatment specially for samples R3, R5 and R6 and it is in agreement with the studies by Jiang et al. [87] and Asadieraghi et al. [41]. The peak at 1730 cm⁻¹ corresponds to C=O stretching vibration of free carbonyl group

therefore it is a typical hemicellulose component. The next peaks from 1650-1510 cm^{-1} shows C=C stretching vibrations of aromatics and generally considered as lignin component. A slight change in intensity of bands around 1730 cm^{-1} and 1650 cm^{-1} of samples R3 and R6 can be observed which is probably due to the high removal of inorganics comparatively. The spectrum around 1400-600 cm^{-1} is very complex to analyze. However, in this region vibrations related to lignin components can be detected as at 1240 cm^{-1} (C=O stretching), 850-750 cm^{-1} (C-H bending). The band between 1440-1400 cm^{-1} contains O-H bending which are related to hemicellulose and cellulose. A band intensity change in this region can be observed in case of sample R6. All above band variations indicate that few changes have occurred in cross linking between different functional groups and thus represents the various acid treatment effects. More significant changes can be observed in case of sample R6.

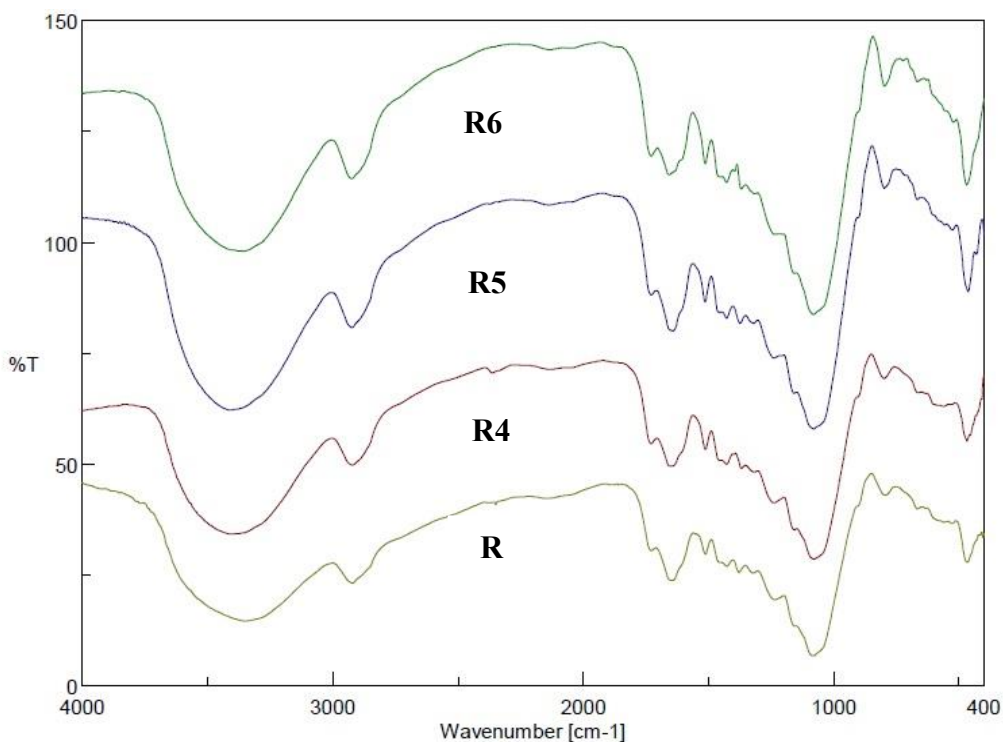


Figure 3.3: FTIR spectra of the raw and H_2SO_4 treated samples

3.3.3 Thermal degradation study

Figure 3.4 shows the thermogravimetric analysis (TGA) curves (percentage weight loss vs temperature) and DTG curves (differential weight loss vs temperature) for raw and treated samples. Three regions are observed in all the curves. The first region from 0 – 100 °C can be assigned to water evaporation. The second region between 250 – 400 °C is attributed to decomposition of cellulose and hemicellulose. The third region between 450 – 500 °C shows the degradation of lignin as found in literature [87]. Further, in the second region, two peaks can be observed. The first peak represents the decomposition of thermally unstable hemicellulose while second peak is showing the degradation of cellulose. It can also be observed that the peaks of treated samples have slightly shifted towards right side showing an increase in temperature as tabulated in Table 3.2. This can be explained by the reason that AAEM, which act as catalyst during decomposition, have been removed through acid treatment and cellulose and hemicellulose are now more resistant towards thermal degradation [101].

Table 3.2: Temperature shift of second shoulder

Sr. No.	Sample ID	Temperature of second shoulder (°C)
1	R	322
2	R1	348
3	R2	351
4	R3	367
5	R4	352
6	R5	358
7	R6	371

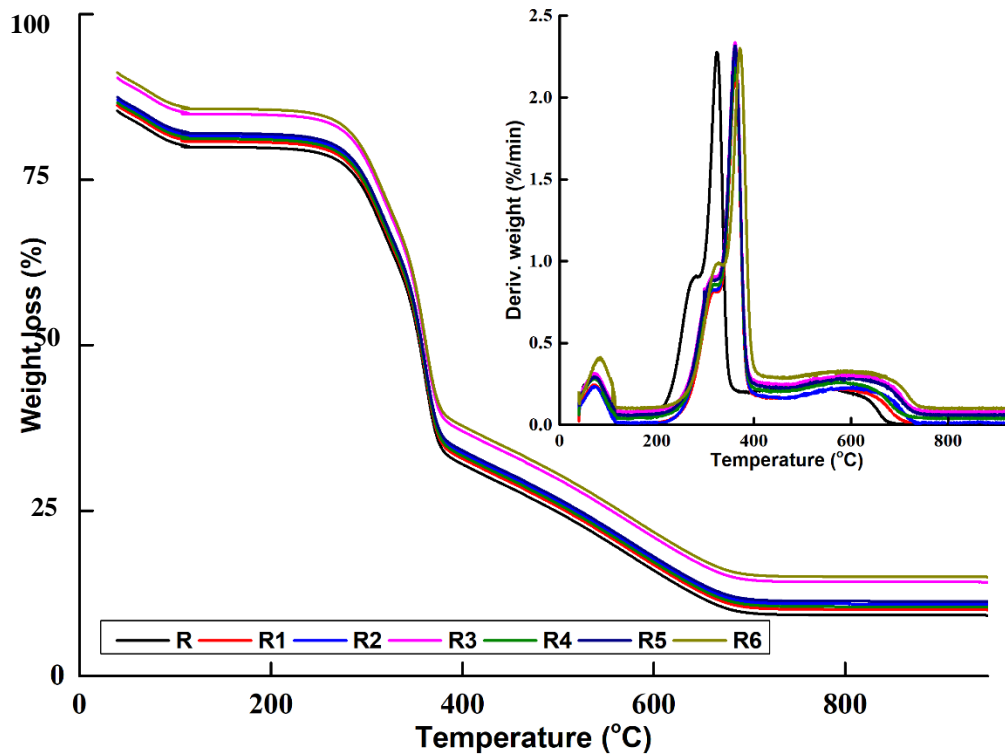


Figure 3.4: Thermogravimetric analysis of raw and acid treated biomass

3.3.4 Ash percentage and heating value

Table 3.3 shows the ash percentage and heating value of all the samples. A maximum decrease of 34.2 % in ash content of sample R6 was observed while a maximum increase of 7.10 % in HHV was observed also for R6. These results are consistent with Carrillo et al [102]. While for R1, R2, R3, R4 and R5 percentage decrease in ash content was 15.6, 17.4, 33, 16.60 and 18.04 %, respectively and percentage increase in heating value was 0.99, 1.53, 5.22, 0.46 and 1.72 %, respectively were observed. As reported for other biomasses, a vivid inverse relation between ash content and heating value was observed as reported by Jenkins et al. In addition, it can also be seen from SEM and FTIR of samples R3 and R6 that both leaching agents comparatively had more effects on the physiochemical structures thus complementing the changes in ash content and HHV of the respective samples.

Table 3.3: Ash content and heating values of untreated and treated samples

Sr. No.	Sample Identification	Ash content (wt. %)	Heating value (MJ/kg)
1	R	15.50	15.07
2	R1	13.08	15.22
3	R2	12.80	15.30
4	R3	10.36	15.90
5	R4	13.00	15.14
6	R5	12.70	15.33
7	R6	10.20	16.14

3.2 Conclusion

Rice husk is suitable for energy generation, however, its slagging nature prevents its use at larger scale. In this experimental work, the changes in physiochemical structural of rice husk using different leaching agents and leaching time intervals were studied. The results showed that leaching performed for 2 hr with H₂SO₄ have removed more AAEM as revealed by the ash content (34.20% decrease) comparatively, however, it has also affected the structure as depicted by SEM and FTIR. The increase of 7.10% in HHV was shown by R6 validating the reciprocal relation between ash content and HHV. The shifting of peaks of treated samples towards high temperature in TG and DTG curves indicated that treated sample are more resistant towards thermal degradation due to the elimination of catalytic role of AAEM.

CHAPTER 4: PHYSIO-CHEMICAL EVALUATION AND THERMAL DEGRADATION STUDY OF TORREFIED INDIGENOUS BIOMASS

4.1 Introduction

For power generation, the most important source in the world is fossil fuel. However, the dependence on fossil fuel is unviable in long run due to their depletion, increase in price and public and political sensitivities to environmental issues. Renewable energy (RE) must be infiltrated into power generation to achieve economic and environmental benefits. RE is energy derived from the resources replenished by nature continually such as sunlight, wind, rain, geothermal heat, biomass, waves and tides [6]. Biomass, a lignocellulosic material, has a great potential to be used as a solid fuel but its inherent properties like hydrophilic nature (water absorbent) and slagging makes it an inefficient fuel at larger scale. High moisture content in raw biomass is one of the most challenging issue as it trims down the efficiency of process and increases the cost. It also leads to low energy density, natural decomposition (fungal attack and biodegradation) and uncertainty in physical, chemical and microbiological properties. High oxygen content than hydrogen and carbon also makes it less efficient for thermochemical conversion processes [10-11]. That is why it is a comparatively inefficient fuel and larger amounts are needed than fossil fuel to get the same amount of energy.

To address the above described challenges and make biomass suitable for energy generation processes, it must be pretreated. Pretreatment process helps in altering the physical properties and chemical compositions of biomass thus making it an efficient fuel. Torrefaction, a thermal pretreatment process, is defined as the thermolysis (slow pyrolysis) of lignocellulosic biomass in temperature ranges of 200-300 °C. The process is carried out at an atmospheric pressure and in inert environment [15,29]. It makes biomass compactable, hydrophobic, grindable, lowers its

oxygen to carbon ratio and increases its heating value thus converting it to an efficient and suitable solid fuel for commercial and residential utilization.

In recent years, biomass torrefaction has attracted more interest to recognize its role in refining the properties of biomass. Yan et al. [38] observed that increase in torrefaction temperature resulted in decrease of mass yield of loblolly pine, but it improved the carbon content of the biomass. Chen et al. [103] torrefied the woody biomass at 220 °C, 250 °C and 280 °C and reported that the torrefaction performed at severe condition increased the higher heating value of the biomass up to 40% however this was achieved at the cost of over 50% of mass lost. Couhert et al. [104] investigated the effect of thermal pretreatment on the production of synthesis gas from gasification of wood. They evaluated that the O/C ratio of the biomass was decreased and the amount of synthesis gas produced increased when torrefaction was performed at intense condition. Rousset et al. [74] studied bamboo thermolysis at three different temperatures and highlighted that the mass yield was less than the energy yield and raising process temperature escalated this difference. Deng et al. [43] evaluated the torrefaction of rape stalk and rice straw for co-gasification. They pointed out that the calorific values of the thermolyzed biomass were increased up to 15% and 17%, respectively, in comparison to native biomasses. The properties of the thermally treated agricultural residues were nearer to that of coal. They also concluded that torrefaction was an auspicious pretreatment process for biomass to integrate with co-gasification of coal.

Pakistan is generating 79% of its total energy from fossil fuel and currently, the electricity shortfall in the country is around 6000 MW [8]. Pakistan has a substantial bio resource base as annual production of agricultural residues is approximately 100 million tons however its contribution to useful energy production is very low [12,105]. Energy crisis in the country had coerced many industries to shut down thus affecting the industrial production and livelihoods of the people [9–

11]. The common perception of energy generation from RE is its cost disadvantage but the escalating prices of fossil fuel in Pakistan and the abundant availability of RE resources may help in addressing the environmental issues and providing a sustainable energy supply [13].

The aim of this study is to investigate the impact of torrefaction, performed at different residence time and temperature, on the indigenous biomass and explore the hydrophilic nature, fuel characteristics, thermal degradation and structural changes in the agricultural residue.

4.2 Materials and Methods

4.2.1 Materials

Raw biomass, Rice Husk was supplied by a local rice mill located in Punjab, Pakistan. The raw material was firstly sieved by using a high vibratory sieve (Model 2Y1237, Sky Machinery) and mass fraction retained between 8 mm and 10 mm screen was selected for torrefaction process. The collected biomass was later washed with distilled water and dried in a rectangular shaped solar greenhouse dryer. The dryer was made up of steel frame with transparent polyethylene walls and roof. Ventilation holes were provided around all sides of the dryer for air circulation. The dried biomass was then stored in air tight bags before any further treatment. N₂ gas (provided by Linde Pakistan Limited) was of analytical grade having 99.999 % purity.

4.2.2 Methods

4.2.2.1 Torrefaction process

Torrefaction process was carried out in a bench scale tube furnace (CARBOLITE CTF 12/TZF 12, Germany). A stainless steel-316 tube (L × D = 300mm × 35mm) was placed in a furnace and suitably connected it with a rotameter and–gas cylinder as shown in Figure 4.1. In a typical experimental run, 10 g of biomass was loaded in the tube and cotton swab was placed on both ends of the tube for even distribution of incoming gas and at the same time hinders the entrainment of biomass with exit gas. Then N₂ gas was purged through packed bed of biomass at a rate of 100

mL/min to uphold an inert environment during torrefaction process. Each biomass sample was heated up at a rate of 10 °C/ min to three different final temperatures i.e. 200, 250 and 300 °C. The biomass sample was kept for four different residence time i.e. 10, 30, 90 and 150 min at each mentioned furnace temperature. After the specified residence time, the tube was cooled down to room temperature while N₂ gas was continuously purging through biomass sample. Later, the torrefied biomass was withdrawn from the tube and its weight was measured. The torrefied biomass was then stored in an air tight bags for further analysis and characterization.

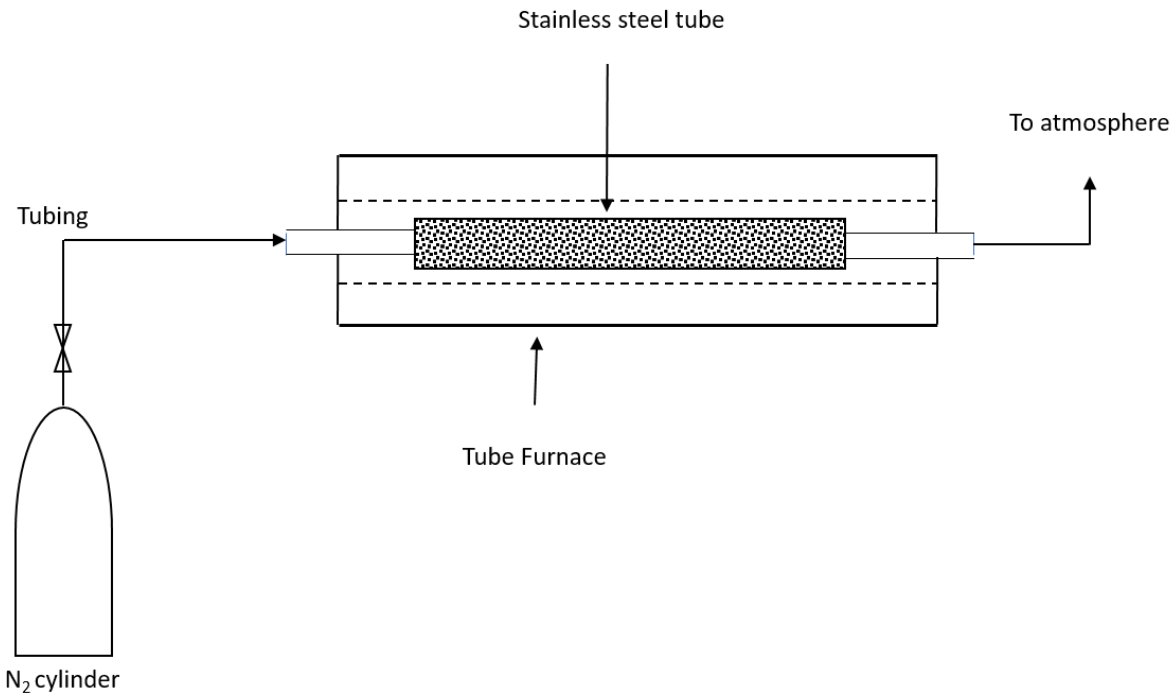


Figure 4.1: Schematic diagram of the torrefaction process

4.2.2.2 Compositional Analysis

To find out the change in weight percentages of C, H, N and S of each sample after torrefaction, ultimate analysis was performed using a Vario Micro Cube, Elementar, Germany. It involves the complete combustion of the sample and converting it to CO₂, H₂O, N₂ and SO₂. Then the gases are separated by chromatography and measured by thermal conductivity probe. Weight percentage of O was calculated by difference. ASTM-3174 was used for the determination of ash content.

4.2.2.3 Calorific Value

The higher heating value (HHV) of raw and torrefied biomass samples was computed according to ASTM D-1989 by using an AC-500 isoperibol calorimeter from LECO. 0.2 g of each biomass sample was loaded in a glass crucible and placed inside the bomb. The bomb was filled with O₂ (99.50%) and placed in water jacket. This assembly was then placed in AC-500 isoperibol calorimeter. After ignition by a pure cotton thread, the sample starts to combust and heat is released which is transferred to the water jacket causing the temperature of water to increase. The HHV of each sample was calculated based on the increase in temperature and expressed in cal.g⁻¹. The ultimate analysis, ash content and HHV determination was repeated twice for each biomass sample and average values are presented.

4.2.2.4 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis was performed to study changes in functional groups of biomass sample after torrefaction using Cary 630 FTIR spectrometer, Agilent. Raw and torrefied biomass samples were individually grounded in a blender. Each sample was placed directly on an Agilent diamond ATR sample interface. A sample press was used to ensure that the samples were in good contact with the sensor surface. Spectral data was collected in the 4000–500 cm⁻¹ region and analyzed using Agilent Microlab software.

4.2.2.5 Water Adsorption

For comparison of hydrophobic behavior of raw and torrefied biomass sample, immersion test is performed. In it, 2 g of each sample was dipped in 500 mL water for 24 hr. After 24 hr, each sample was filtered and its weight was determined.

4.2.2.6 Thermal Degradation Study

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves for raw and torrefied biomass samples were drawn by using a Thermogravimetric Analyzer SDT Q600 from TA Instruments. 10 mg of each sample was taken in a platinum crucible and placed in the furnace of SDT Q600 TA instrument. It was initially heated up to 105 °C in the presence of N₂ gas. The temperature was held constant at 105 °C for 5 min for moisture evaporation. Then temperature was raised to 500 °C in N₂ gas environment. To ensure complete combustion, the heating was continued for 10 min at 950 °C in the presence of O₂. The heating rate for all cases was set at 10 °C/min.

4.2.2.7 Scanning Electron Microscopy (SEM)

To examine the surface morphology of torrefied biomass, all samples were observed by SEM (JEOL JSM-6490 LV) operating at low vacuum and 5 kV accelerating voltage. All the samples were spread on an adhesive carbon tape attached with a sample tab and sent into the SEM for scanning. The images are magnified by factor of 1 k to exhibit the micro structure of the biomass cross sections.

4.3 Results and Discussion

4.3.1 Ultimate analysis and ash content

The ultimate analysis was performed to evaluate the efficacy of torrefied biomass samples as solid fuel. It determines the elemental composition (weight percentages) of samples which are presented in Figure 4.2 along with ash content. With increasing process severity (i.e. residence time and

temperature), the thermal degradation of biomass resulted in higher carbon (C) and ash content and the weight percentages of oxygen (O) and hydrogen (H) showed a declining trend. In non-oxidative torrefaction environment, the major mechanisms for thermal degradation of biomass samples are devolatilization and slow pyrolysis. Lower oxygen and hydrogen content in thermolyzed biomass samples indicate the removal of light volatiles and moisture and diminution of hemicellulose [66,106].

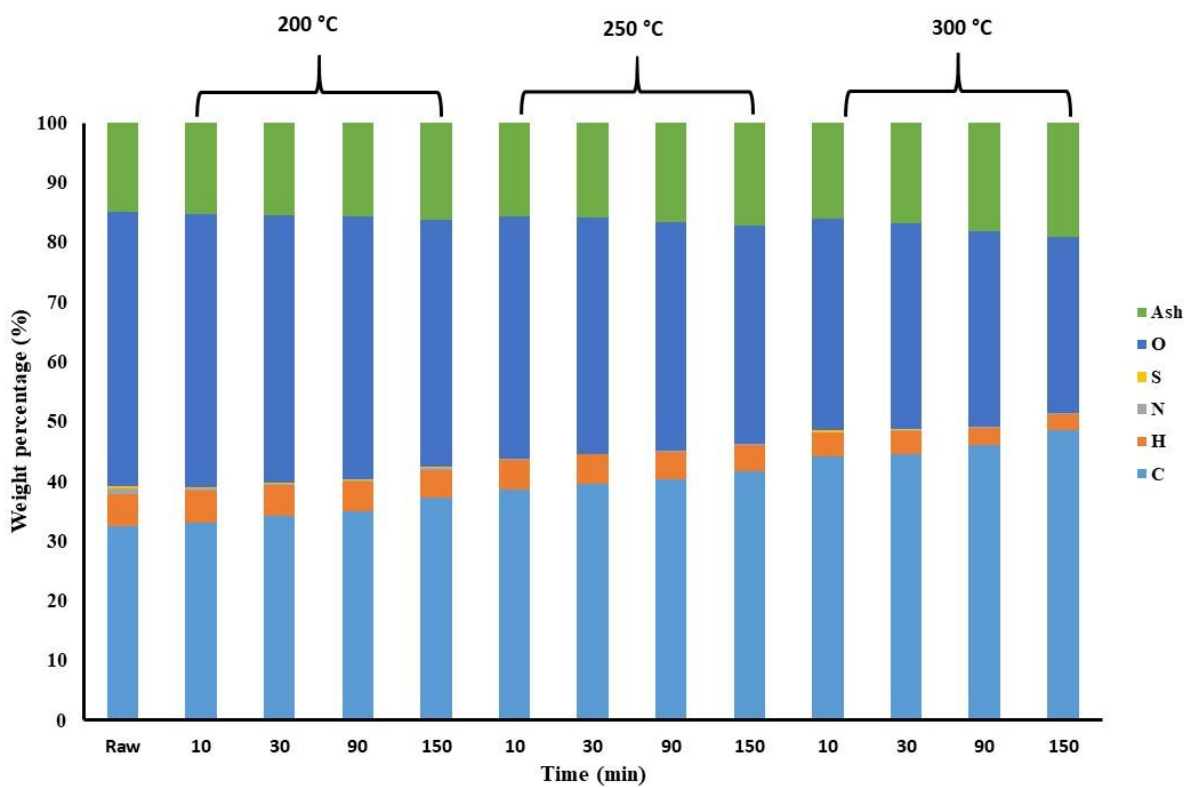


Figure 4.2: Elemental analysis of raw and torrefied biomass samples

Torrefaction emanated in increased C content which upsurges the energy value of biomass. The maximum value of C is observed for sample treated at 300 °C for 150 min i.e. 48.46%. The maximum decrease in O content of torrefied biomass samples is calculated as 29.61%. This reducing trend improves the fuel quality of biomass as higher O content increases the moisture absorption capacity of samples thus reducing the shelf life. The decline in weight percentages of

N and S is very small however this aversion adds the value to biomass as N decreases the heating value and S causes the corrosion of equipment and pollution.

4.3.2 Mass and energy yields

Empirical formula of a compound shows the ratios of elements present in a compound and helps in understanding the elemental analysis. The empirical formulas of the raw and torrefied biomass samples are expressed in Table 4.1. The H is very high in native biomass sample than C while O and C are comparable. The higher amounts of O and H makes the raw biomass hygroscopic. After the thermal treatment, a gradual decrease in the atomic H and atomic O can be observed thus improving the fuel properties of biomass samples. The sample torrefied at 300 °C for 150 min demonstrates empirical formula as $\text{CH}_{0.68}\text{O}_{0.46}$ which clearly reflects that once torrefaction operating conditions are becoming acute, the torrefied biomass samples tends towards coal characteristics. The empirical formula of the bituminous coal is $\text{CH}_{0.81}\text{O}_{0.08}$ as reported by Chen et al. In the reported literature, it is shown that the coal has lower percentage of atomic oxygen compared to other constituents while atomic hydrogen and carbon are proportioned almost equivalently. These characterization results supported that the torrefied biomass could serve as an efficient solid.

Table 4.1: Mass and energy yield and HHV of raw and torrefied biomass samples

Temperature (°C)	Time (min)	Mass yield (wt. %)	Energy yield (%)	HHV (cal.g ⁻¹)	C _x H _y O _z
Raw		100	100	3939	CH _{2.01} O _{1.06}
	10	95.03	96.79	4012	CH _{1.93} O _{1.03}
200	30	93.28	96.15	4135	CH _{1.65} O _{0.97}
	90	92.28	94.92	4254	CH _{1.64} O _{0.94}
	150	90.06	91.86	4339	CH _{1.52} O _{0.84}
	10	93.07	96.88	4100	CH _{1.56} O _{0.79}
	30	87.92	93.04	4199	CH _{1.46} O _{0.75}
	90	82.05	83.80	4288	CH _{1.38} O _{0.71}
250	150	77.05	78.15	4350	CH _{1.29} O _{0.66}
	10	56.18	60.20	4221	CH _{1.05} O _{0.60}
	30	54.97	58.04	4457	CH _{1.01} O _{0.58}
	90	49.03	51.32	4665	CH _{0.76} O _{0.53}
300	150	48.46	51.03	4913	CH _{0.68} O _{0.46}

For evaluation of torrefaction of biomass, the mass yield (MY) and energy yield (EY) are the most critical parameters. Table x shows the mass and energy yield and HHV of raw and torrefied biomass samples. The MY and EY were estimated based on:

$$MY = (m_{\text{torr}}/m_{\text{feedstock}}) * 100$$

$$EY = MY * (HHV_{\text{torr}}/HHV_{\text{raw}})$$

Where m_{torr} and $m_{\text{feedstock}}$ are the mass yield of biomass after torrefaction, and before torrefaction measured in grams and HHV_{torr} and HHV_{raw} are the heating values of torrefied and raw biomass samples estimated in cal/g respectively. As the torrefaction temperature is increased, there is a diminution in mass yield of the samples. At 200 °C, the decline in mass yield ranges from 95.03% to 90.06% which is caused by the limited decomposition of lignin and the elimination of low molecular weight aromatic compounds [107]. When the process temperature is raised, the reduction in mass yield becomes more distinct and ranges from 93.07% to 77.05% for 250 °C and

56.18% to 48.46% for 300 °C. The reason for this dramatic decline is the degradation of hemicellulose and limited decomposition of lignin and cellulose [108]. The mass yield of torrefied biomass samples decreases with increase in residence time from 10 min to 150 min. However, the effect of residence time on the mass yield is less extensive for the biomass samples torrefied at 200 °C and 300 °C, in contrast to temperature, as the reduction in mass yield is 4.97 % and 7.72 % respectively. On the other hand, the reduction in mass yield is more significant i.e. 16.02 % when the temperature is set at 250 °C. It is because of the fact that hemicellulose decomposition rate is higher at 250 °C with increase in the residence time [109]. At this temperature, hemicellulose follows depolymerization and devolatilization mechanisms for its degradation. The HHV values of the torrefied biomass samples increases, a trend similar to the results reported for bamboo torrefaction by Rousset et al. [74]. The HHV values increased from 3939 cal.g⁻¹ to 4339, 4350 and 4913 cal.g⁻¹ for biomass samples torrefied at 200 °C, 250 °C and 300 °C respectively. The maximum value of HHV is observed at 300 °C and 150 min i.e. 4913 cal.g⁻¹ which is in agreement to the observed values of higher carbon, lower H/C and O/C atomic ratios than the other torrefied biomass samples. As expected, the energy yield decreases with increase in temperature as it depends on mass yield and increase in HHV. The maximum energy yield is obtained for the biomass torrefied at 200 °C for 10 min i.e. 96.80% and minimum energy yield is observed for the biomass torrefied at 300 °C for 150 min i.e. 51%. The energy yield of the remaining torrefied biomass samples ranges from 51 - 96.8%. In spite of the fact that torrefaction performed under severe conditions increased the HHV of the torrefied biomass samples, a substantial amount of energy is forfeited due to loss of mass which explains the decrease in energy yield.

4.3.3 FTIR

Every molecule shows a unique spectrum after the absorption of infrared rays based on its natural frequency of vibration. FTIR spectroscopy feats this fact and helps in assessing the structure and

structural changes which are caused by the thermal treatment in present investigation. Figures 4.3, 4.4 and 4.5 show the FTIR spectra of torrefied biomass at examined temperatures under different exposure times in reference to raw biomass sample. In native biomass, a strong O–H stretching absorption is seen at 3329 cm^{-1} and a conspicuous C–H stretching absorption at 2907 cm^{-1} can be assigned to aliphatic chain. There are many clear peaks in the fingerprint region between 1750 and 700 cm^{-1} . These peaks can be ascribed as 1731 cm^{-1} for unconjugated C=O in hemicellulose, 1633 cm^{-1} for absorbed O–H and conjugated C–O, 1508 cm^{-1} for aromatic skeletal in lignin, 1455 cm^{-1} and 1423 cm^{-1} for C–H twisting vibrations in lignin and carbohydrates, 1376 cm^{-1} for C–H deformation in hemicellulose and cellulose, 1315 cm^{-1} for C–H vibration in cellulose in syringyl derivatives, 1235 cm^{-1} for syringyl ring and C–O stretch in xylan and lignin, 1039 cm^{-1} for C–O stretch in hemicellulose and cellulose and 885 cm^{-1} for C–H wagging vibrations in cellulose [110].

The peak intensity of O–H band around 3329 cm^{-1} weakens with rise in residence time at all observed temperatures however at $200\text{ }^{\circ}\text{C}$ the decrease in peak intensity is less in comparison to other two thermal degradation temperatures i.e. $250\text{ }^{\circ}\text{C}$ and $300\text{ }^{\circ}\text{C}$. It can also be observed from the Figure 4.5 that the peak for hydroxyl functional group almost diminishes for 90 min or higher residence time. This was primarily engendered by loss of water and hydrogen bonds resulting from dehydroxylation of hemicellulose and degradation of cellulose [74,111]. The rapidity with which peak intensity drops down during the torrefaction of biomass at $300\text{ }^{\circ}\text{C}$ reflects that the dehydroxylation reaction rate pace up at elevated temperatures [74,110–112]. In the same spectrum (Figure 4.5) the change of peak intensity at 2907 cm^{-1} is probably due to decarboxylation reactions in the biomass substrate those are occurred possibly because of degradation in the cellulose and hemicellulose [112–114]. Its disappearance explicates the severe disruption of cellulose and hemicellulose. The scission of aliphatic chain may produce CH_4 , C_2H_4 and C_2H_6 in gaseous

products. The disappearance of peak at 1338 cm^{-1} and 1302 cm^{-1} can also be observed in Figure 4.5 while it is present in Figure 4.3 and 4.4. These peaks show the C-H in plane bending and CH_2 wagging in cellulose. Their disappearance clearly shows that when torrefaction is carried out at $300\text{ }^\circ\text{C}$, it sternly rattled the cellulose following decarboxylation reactions [111]. Comparing the spectrum between 1970 to 2030 cm^{-1} in the Figures 4.3, 4.4 and 4.5 show that the peak becomes prominent in Figure 4.5 compared to other samples. It can probably be associated to overtone in the–aromatic rings of lignin [113]. Disruption of cellulosic structure is higher at elevated temperatures hence making the overtone noticeable due to prevalence of lignin in the biomass. All the structural changes reported are the attributes of torrefaction process generated from its deoxidation effect and were conducive to the efficient use of biomass for energy generation.

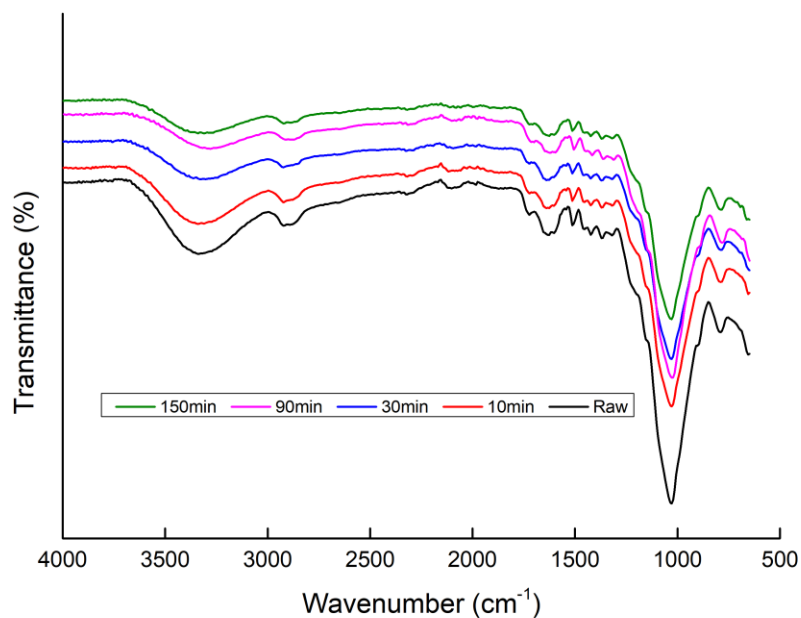


Figure 4.3: FTIR spectrum of raw and torrefied biomass ($200\text{ }^\circ\text{C}$)

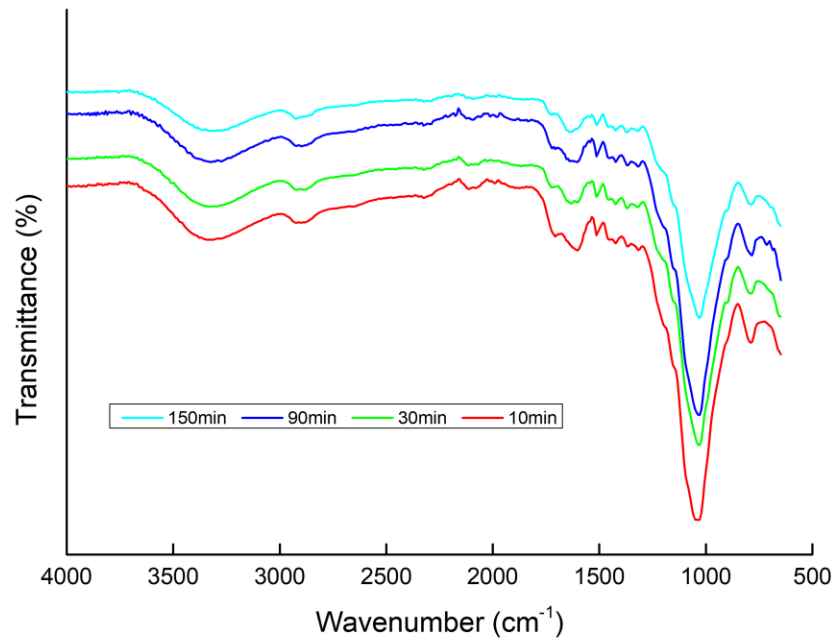


Figure 4.4: FTIR spectrum of raw and torrefied biomass (250 °C)

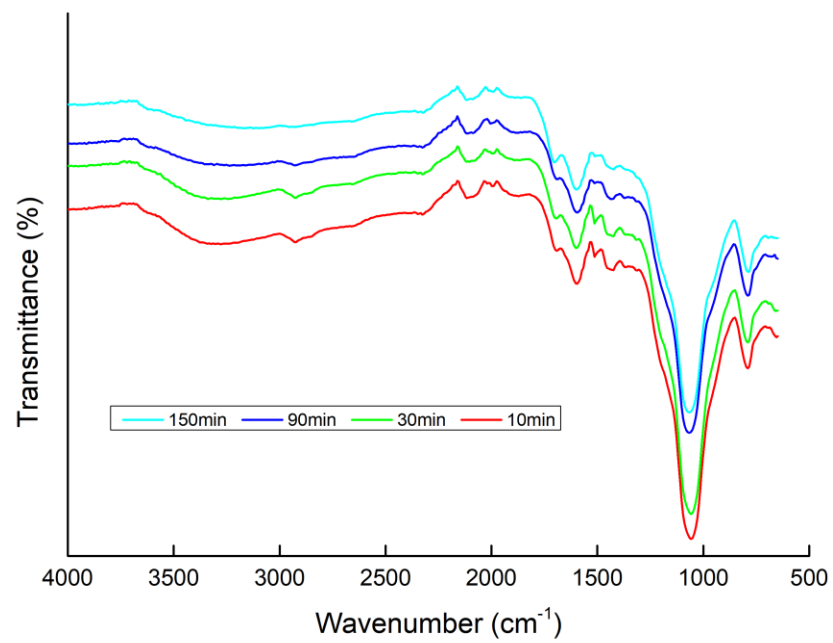


Figure 4.5: FTIR spectrum of raw and torrefied biomass (300 °C)

4.3.4 Hydrophobic Characteristic

One of the main drawbacks of biomass is its affinity towards moisture which degenerate its performance particularly related to thermochemical processes such as combustion and gasification. The hydrophobic nature of treated biomass was observed and each sample was examined through immersion test. The ability of moisture absorption of all the samples is presented in Figure 4.6 in terms of percent increase in weight. The tendency of moisture absorption-of thermalized samples is comparatively lower than the virgin biomass which probably because of de-polymerization of long chain polysaccharides molecules. The raw biomass sample shows a highest increase in weight i.e. 308% after water immersion which reflects its handling difficulty-during its transportation and storage. The water absorption trend shown by torrefied biomass samples also varies with respect to different process parameters. The absorption capability of samples torrefied at higher temperature and residence time is lower and the minimum water absorption is observed for the biomass thermolyzed at 300 °C for 150 min i.e. 92%. The remaining samples shows decrease in water absorption from 284-96%. When temperature is increased in excess of 200 °C, release of bounded water in biomass and thermal degradation of hemicellulose takes place. This is consorted with limited carbonization and devolatilization of cellulose and lignin. These non-reversible changes introduce the hydrophobic behavior in torrefied biomass samples and increased its stability and durability [23,84,115]. The ignition temperature of biomass was also reduced by these structural changes [72].

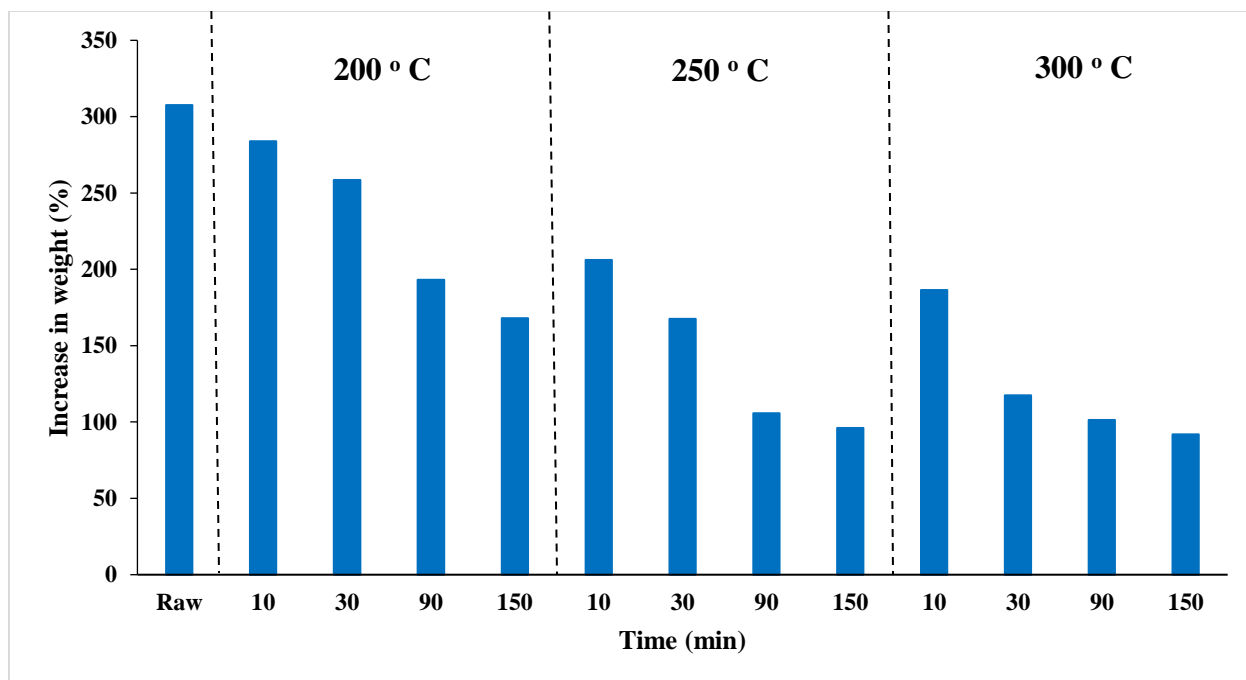


Figure 4.6: Water uptake by raw and torrefied biomass

4.3.5 Thermal degradation study

A study to inspect the thermal degradation of torrefied biomass samples was carried out. The thermogravimetric curves (TG) and derivative thermogravimetric curves (DTG) for raw and samples thermolyzed at 200, 250 and 300 °C for 10 and 150 min are presented in the Figure 4.7. In virgin biomass, three distinct stages of weight loss can be observed which are also recognizable by the peaks in DTG curves. The first stage (< 200 °C) in TG curve is attributed to the moisture loss and light volatile removal and the same change can also be observed in DTG curve. The next stage (270-400 °C) stems from the thermal degradation of hemicellulose and cellulose. In DTG curve, this stage can be distinguished by a central peak having two shoulders. The first shoulder represents the thermal decomposition of hemicellulose and the second shoulder represents the thermal degradation of the cellulose [116]. The third stage (420-500 °C) shows the degradation of lignin.

For second stage, the decay in weight decreasing profiles of the virgin biomass and samples torrefied at lower temperature and residence time is sharp and this region is attributable to hemicellulose degradation. A delay in the second stage is observed for samples thermolyzed at higher temperature and time which shows the removal of hemicellulose after intense torrefaction. This is because of the dehydroxylation of hemicellulose in these samples which is also consistent with the observation from FTIR spectrum. It may be concluded that during torrefaction, the most reactive segment (hemicelluloses) is affected, while the others remain stable.

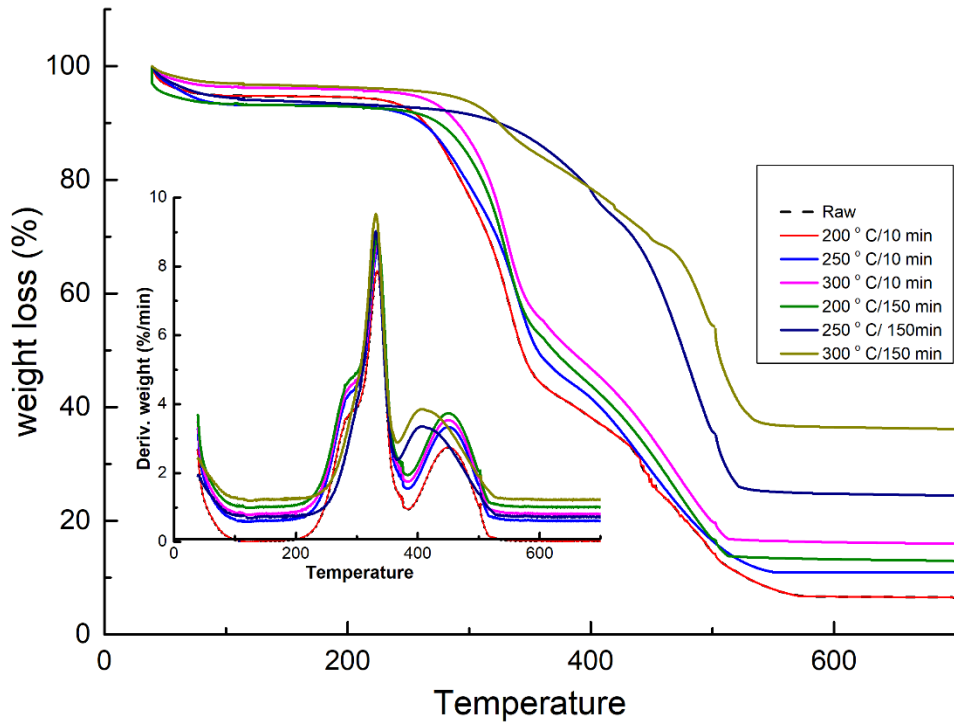


Figure 4.7: Thermogravimetric analysis of raw and torrefied biomass

4.3.6 Morphological features

The SEM micrographs of the raw and torrefied biomass are shown in Figure 4.8. Rice husk is a lignocellulosic material and an agricultural biomass residue having lamina structure. The epidermis of the rice husk is formed by aligned and symmetrical bumps composed mainly of silica onto the cellulose [117]. The embossed conoids can also be observed at the surface. It was observed that the thermal treatment affected the biomass structure, mainly destroying the fibrous anatomy and pertinacity of biomass. Although the lamina structure was maintained by the thermalized samples however destructed conoids, cracks and swollen bumps can be observed in the biomass surface. The damage to biomass structure becomes more pronounced in comparison to virgin sample as process conditions are intensified. This ruination agrees with the higher release of volatile matter, dehydroxylation of hemicellulose and thermal degradation of cellulose [106].

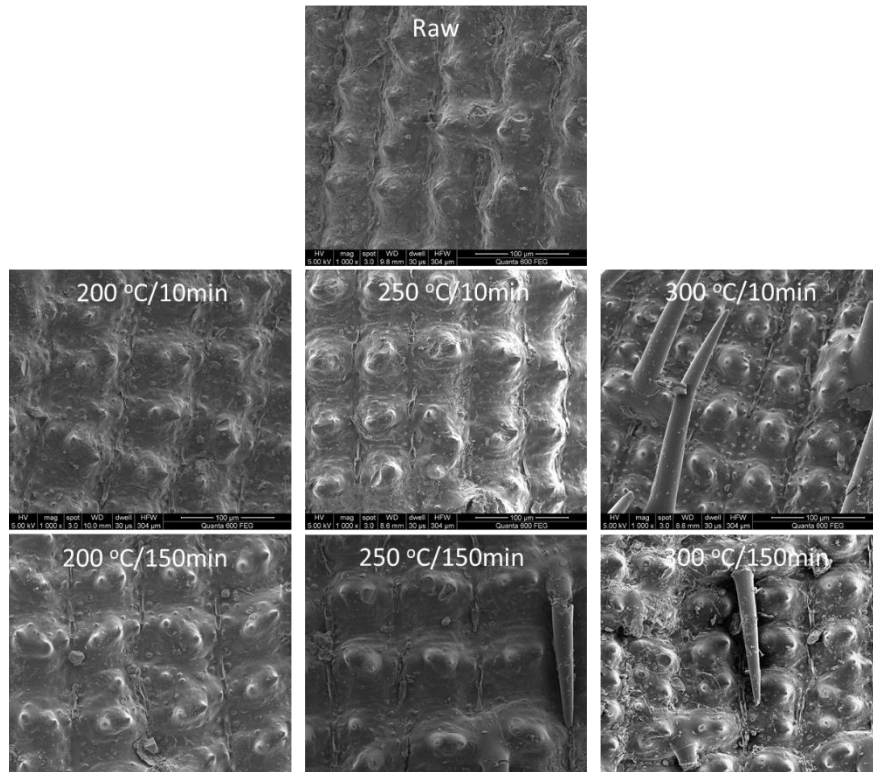


Figure 4.8: SEM micrographs of raw and torrefied biomass samples for different torrefaction temperatures and residence time

4.4 Conclusion

Indigenous biomass can be turned into more improved solid fuel after torrefaction as thermolyzed samples showed higher carbon contents as compared to its raw counterpart. The thermal treatment also reduces the H/C and O/C ratios in biomass because of devolatilization and dehydroxylation of hemicellulose hence bringing it nearer to coal in terms of fuel quality. At intense process conditions, more ruination to the structure of thermolyzed samples can be observed which demonstrates the thermal degradation of hemicellulose and evolution of volatile matter as revealed through SEM photomicrographs. The higher heating value of thermolyzed samples improve upto 4913 cal.g^{-1} as compared to raw biomass of 3939 cal.g^{-1} however the mass and energy yield decreases especially at severe torrefaction condition i.e. $300 \text{ }^{\circ}\text{C}/150 \text{ min}$. The FTIR spectrum showed reduction in the O–H peak intensity, which can be verified by the reduction in H/C and O/C ratios, due to dehydroxylation of hemicellulose thus improving the hydrophobic nature of biomass. Thermal degradation analysis of torrefied biomass showed three distinct stages of weight loss for all samples. The hemicellulose is the fraction more affected during the torrefaction as observed in the DTG curves. On the overall, torrefaction not only improved the fuel characteristics of biomass but also made it hydrophobic thus making it an alternative fuel that may be used at commercial level for energy generation.

CHAPTER 5: EFFECT OF PRETREATMENT PROCESSES ON FUEL CHARACTERISTICS OF BIOMASS

5.1 Introduction

Pakistan is rich in production of biomass because of appropriate growing environment and fertile land. Being an agricultural country, nearly 62% of the country's population resides in rural areas, and is directly or indirectly linked with agriculture for their livelihood. Rice husk is a lignocellulosic source and its annual production is 100 million tons per year [12]. This agricultural residue can be converted into energy by application of thermo-chemical process such as combustion [118,119], pyrolysis, gasification [119,120] and liquefaction [121,122]. Among all thermochemical process, no process is a superior option over others. Liquefaction and pyrolysis produce a liquid fuel, however, high pressure requirement in liquefaction makes it a sophisticated for thermochemical conversion of biomass [122] and production of low quality bio oil from pyrolysis limits its application to combustion or as densification to minimize transportation cost of biomass [123,124]. The inherent properties of agricultural residue like high moisture content and slagging makes it an inefficient fuel due to which larger amounts are needed than fossil fuel to get the same amount of energy. High moisture content in biomass is due to its hydrophilic nature. It decreases the process efficiency and increases the cost. It also leads to low energy density, natural decomposition (fungal attack and biodegradation) and uncertainty in physical, chemical and microbiological properties [15]. Mineral matter is also present in the biomass in the form of alkali and alkaline earth metals (AAEM). The melting points of AAEM are lower than the usual combustion temperatures. At their melting points, they capture the carbon, deposit on the heat exchanger surfaces and make an insulative layer (slag) which reduces the heat transfer [41]. To address the above described issues and make biomass an efficient fuel, it must be pretreated.

Demineralization is defined as the acid leaching of biomass and weak solutions of strong acids are used for this purpose. The amount of AAE in biomass ranges from <1% to 20%, depending on the biomass species [90,125]. The effects of inorganic metals present in biomass on its thermal degradation have been comprehensively studied by researchers [40,126,127]. They mostly pointed out that the presence of AAEM forms a slag on the heat transfer surface and catalyze the biomass thermochemical conversion. Torrefaction is the thermal treatment of biomass in temperature range of 200–300 °C. It is performed at atmospheric pressure and requires an inert environment. Chen et al. [103] torrefied the woody biomass at 220 °C, 250 °C and 280 °C and reported that the torrefaction performed at severe condition increased the higher heating value of the biomass up to 40% however this was achieved at the cost of over 50% of mass lost. Couhert et al. [104] investigated the effect of thermal pretreatment on the production of synthesis gas from gasification of wood. They evaluated that the O/C ratio of the biomass was decreased and the amount of synthesis gas produced increased when torrefaction was performed at intense condition. Rousset et al. [74] studied bamboo thermolysis at three different temperatures and highlighted that the mass yield was less than the energy yield and raising process temperature escalated this difference. The focus of this work is to highlight the impacts of torrefaction on demineralized rice husk and explore its hydrophilic and slagging nature.

5.2 Materials and Methods

5.2.1 Materials

Biomass used for this study is rice husk supplied by a local rice mill, situated in Gujranwala, Punjab. The biomass was sieved using a high vibratory sieve (model 2Y1237, Sky machinery) and fraction between 8 mm and 10 mm was selected for torrefaction process. The biomass was washed with distilled water and dried in rectangular shaped solar greenhouse dryer. The dryer has steel frame with transparent polyethylene walls and roof. Ventilation holes were present on all sides of

the dryer for air circulation. The dried biomass was then stored in air tight bags before any further treatment. N₂ gas (provided by Linde Pakistan Limited) used was of analytical grade having 99.999% purity.

Dilute solution (5 weight percent) of strong acids i.e. HCl (Riedel-deHaën) and H₂SO₄ (Riedel-deHaën) were used as leaching agents.

5.2.2 Methods

5.2.2.1 Demineralization Process

Firstly, the rice husk was washed with distilled water and dried in a rectangular shaped solar greenhouse dryer. The dryer was made up of steel frame with transparent polyethylene walls and roof. Ventilation holes were provided around all sides of the dryer for air circulation. Then the demineralization of the biomass was conducted using 5 weight percent solutions of H₂SO₄. The solid to liquid ratio (biomass to leaching agent) was 1:15. The mixtures of rice husk and leaching agents were thoroughly mixed with the help of an orbital shaker at 200 rpm for 120 min at room temperature. The treated biomass samples were then washed with deionized water until the pH value approached to neutral. After washing, treated samples were dried in oven at 60 °C for 24 h and then were stored in air tight bags for further treatment, characterization and analysis.

5.2.2.2 Torrefaction Process

Torrefaction process was carried out in a bench scale tubular reactor. It includes a tube furnace model CARBOLITE CTF 12/TZF 12, Germany, a stainless steel-316 tube (300mm in length, 35mm in diameter), a rotameter and a gas cylinder. In a typical experimental run, 10 g of the demineralized biomass was loaded in the tube and cotton swab was placed on both ends of the tube for even distribution of N₂ and to hinder the entrainment of biomass with N₂. Then N₂ was purged at 100 mL/min to uphold an inert environment. Each biomass sample was heated up at a heating rate of 10 °C/ min to 275 °C. At these temperatures, biomass was kept for 30 min. After the

specified residence time, the tube was cooled down with continuous purge of N₂ to room temperature. The torrefied biomass was withdrawn from the tube and its weight was measured. The treated specimen was then stored in air tight bags for further analysis and characterization.

5.2.2.3 Compositional Analysis

The elemental composition of the treated biomass samples was determined using elemental analyzer, vario MICRO cube, Elementar, Germany. The rice husk samples were dried at 60 °C and grounded using a mortar and pestle to have a homogeneous powder. 0.25 mg sample was taken in a tin capsule and placed it in an auto-sampler for analysis. Weight percentage of O was calculated by difference. ASTM-3172 was used for the determination of volatile matters, fixed carbon and ash content.

For the quantification of the mineral content present in the rice husk, a XRF analyzer (using PANalytical 2830 ZT WD) was used. The analyzer includes a 4-watt, 50 kV X-ray tube. The specimen pellet was made by mixing sample (75%) and wax (25%). The slagging factor was estimated using the following equation;

$$\text{Slagging factor} = \frac{(Fe_2O_3 + Na_2O + CaO + MgO + K_2O)}{(SiO_2 + Al_2O_3)}$$

The metal oxide in the above equation represents its weight percentage in the biomass.

5.2.2.4 Calorific Value

The higher heating value (HHV) of raw, demineralized and demineralized and torrefied biomass samples was computed according to ASTM D-1989 by using an AC-500 isoperibol calorimeter from LECO. 0.2 g of each biomass sample was loaded in a glass crucible and placed inside the bomb. The bomb was filled with O₂ (99.50%) and placed in water jacket. This assembly was then placed in AC-500 isoperibol calorimeter. After ignition by a pure cotton thread, the sample starts to combust and heat is released which is transferred to the water jacket causing the temperature of water to increase. The HHV of each sample was calculated based on the increase in temperature

and expressed in cal.g^{-1} . The ultimate analysis, ash content and HHV determination was repeated twice for each biomass sample and average values are presented.

5.2.2.5 Water Absorption

For comparison of hydrophobic behavior of raw, demineralized and demineralized and torrefied biomass samples, immersion test is performed. In a typical run 2 g of each sample was dipped in 500 mL water for 24 hr at room temperature. After a day, each sample was filtered and its weight was determined.

5.2.2.6 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis was performed to study changes in functional groups of biomass sample after torrefaction using Cary 630 FTIR spectrometer, Agilent. Raw and torrefied biomass samples were individually grounded in a blender. Each sample was placed directly on an Agilent diamond ATR sample interface. A sample press was used to ensure that the samples were in good contact with the sensor surface. Spectral data was collected in the $4000\text{--}500\text{ cm}^{-1}$ region and analyzed using Agilent Microlab software.

5.2.2.7 Thermal Degradation Study

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves for raw and torrefied biomass samples were drawn by using a Thermogravimetric Analyzer SDT Q600 from TA Instruments. 10 mg of each sample was taken in a platinum crucible and placed in the furnace of SDT Q600 TA instrument. It was initially heated up to $105\text{ }^{\circ}\text{C}$ in the presence of N_2 gas. The temperature was held constant at $105\text{ }^{\circ}\text{C}$ for 5 min for moisture evaporation. Then temperature was raised to $500\text{ }^{\circ}\text{C}$ in N_2 gas environment. To ensure complete combustion, the heating was continued for 10 min at $950\text{ }^{\circ}\text{C}$ in the presence of O_2 . The heating rate for all cases was set at $10\text{ }^{\circ}\text{C}/\text{min}$.

5.3 Results and Discussion

5.3.1 XRF analysis

For the estimation of the inorganic content in the virgin and acid treated samples, XRF analysis was performed. The decline in the weight percentages of the inorganic components (K, Ca, Mg, P, Na, S and Fe) of the biomass is observed after the acid leaching as shown in Figure 5.1. The amount of minerals removed is most likely linked with the solubility of the different metal oxides in H_2SO_4 solution [128]. The major inorganic constituents effectively removed by the leaching agent from the biomass are CaO, K_2O , SO_3 , P_2O_5 and Na_2O . The acid treatment decreased the MgO, P_2O_5 , SO_3 , K_2O , CaO, MnO, Fe_2O_3 , ZnO and Na_2O in the biomass by 83%, 12%, 70%, 78%, 80%, 69%, 88%, 23% and 85% respectively. The removal of AAEM also resulted in the reduction of slagging factor from 0.8 – 0.1. The decrease in the mineral content and slagging factor will reduce the slag formation on the heat transfer surface and walls of the heat exchange equipment thus improving the fuel quality of the biomass [129].

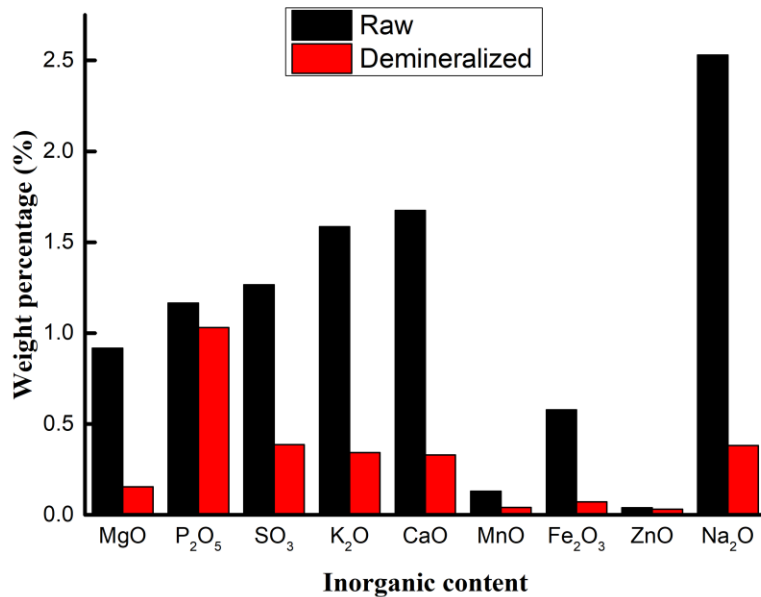


Figure 5.1: XRF analysis

5.3.2 Proximate and ultimate analysis

Proximate analysis of virgin, demineralized and demineralized and torrefied samples are presented in Table 1. Compared to raw biomass, a significant decrease i.e. 18 - 11.03 wt% in ash content of demineralized samples is observed however the acid treatment also increased the volatile matter from 62.74% to 67.43%. The torrefaction of the demineralized biomass reduces the volatile matter to 50.22% and raised the fixed carbon content to 30.20% in comparison to the native biomass having 62.74% volatile matter and 19.26% fixed carbon. The higher content of fixed carbon and reduced ash content mean that the demineralized and thermolyzed biomass has more energy potential and can prevent the equipment from the serious problems of slagging and corrosion [62,130].

Table 5.1: Proximate analysis (moisture free basis, wt%), ultimate analysis (wt%) and HHV of raw and treated samples

Biomass sample	Fixed Carbon (%)	Volatile matter (%)	Ash Content (%)	HHV (cal.g⁻¹)
Raw	19.26	62.74	18.00	3939
Demineralized	21.54	67.43	11.03	4176
Demineralized and torrefied	30.20	50.22	19.58	4356

The ultimate analysis was performed to assess the efficiency of the demineralized and thermolyzed biomass samples as solid fuel. It determines the elemental composition (weight percentages) of samples which are presented in Figure 5.2. After demineralization, the carbon content increases from 32.45% to 34.87% while the ash content decreases from 15.30% to 11.03%. The torrefaction of the demineralized biomass resulted in higher carbon content (32.45% to 43.10%) and the weight percentages of oxygen and hydrogen showed a decreasing behavior from 45.92% to 36.08% and

5.44% to 4.30% respectively. In non-oxidative torrefaction environment, the major mechanisms for the thermal degradation of the biomass samples are devolatilization and slow pyrolysis.

The lower oxygen (O) and hydrogen (H) content in the thermolyzed biomass samples indicate the evolution of light volatiles and moisture and destruction of hemicellulose [66,106]. This reducing trend improves the fuel quality of biomass as higher O content increases the moisture absorption capacity of samples thus reducing the shelf life. The decline in weight percentages of nitrogen (N) and sulfur (S) is very small however this aversion adds the value to the biomass as N decreases the

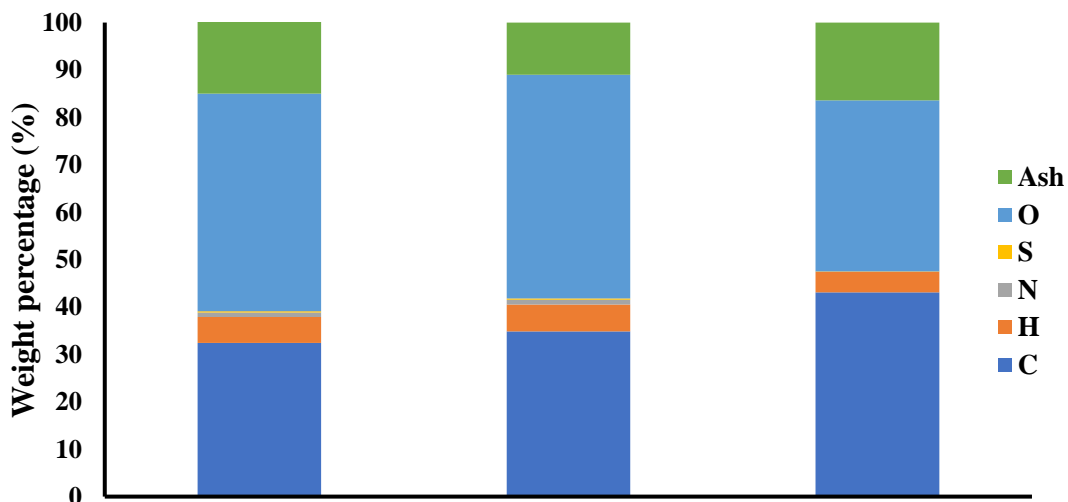


Figure 5.2: Compositional analysis

heating value and S causes the corrosion of equipment and pollution. The HHV values of the treated biomass samples significantly increases as tabulated in Table 5.1. The HHV values increased from 3939 cal.g⁻¹ to 4176 cal.g⁻¹ and 4356 cal.g⁻¹ in case of demineralized and demineralized and torrefied samples respectively. The increase in HHV agrees to the observed values of higher carbon content.

5.3.3 Hydrophobic characteristic

One of the main drawbacks of biomass is its affinity towards moisture which degenerate its performance particularly related to thermochemical processes such as combustion and gasification. The hydrophobic nature of treated biomass was observed and each sample was examined through immersion test. The ability of moisture absorption of all the samples is presented in Figure 5.3 in terms of percent increase in weight. The tendency of moisture absorption-of thermalized samples is comparatively lower than the virgin and acid treated biomass samples which probably because of de-polymerization of long chain polysaccharides molecules. The raw biomass sample shows a highest increase in weight i.e. 308% after water immersion which reflects its handling difficulty during its transportation and storage while the weight of demineralized biomass after water adsorption increases by 304%. The absorption capability of acid treated samples torrefied at 275 °C is lower i.e. 140%. The thermal treatment releases the bounded water in the biomass and the thermal degradation of hemicellulose takes place. This is consorted with limited carbonization and devolatilization of cellulose and lignin. These non-reversible changes introduce the hydrophobic behavior in torrefied biomass samples and increased its stability and durability [23,84,115]. The ignition temperature of biomass was also reduced by these structural changes [72].

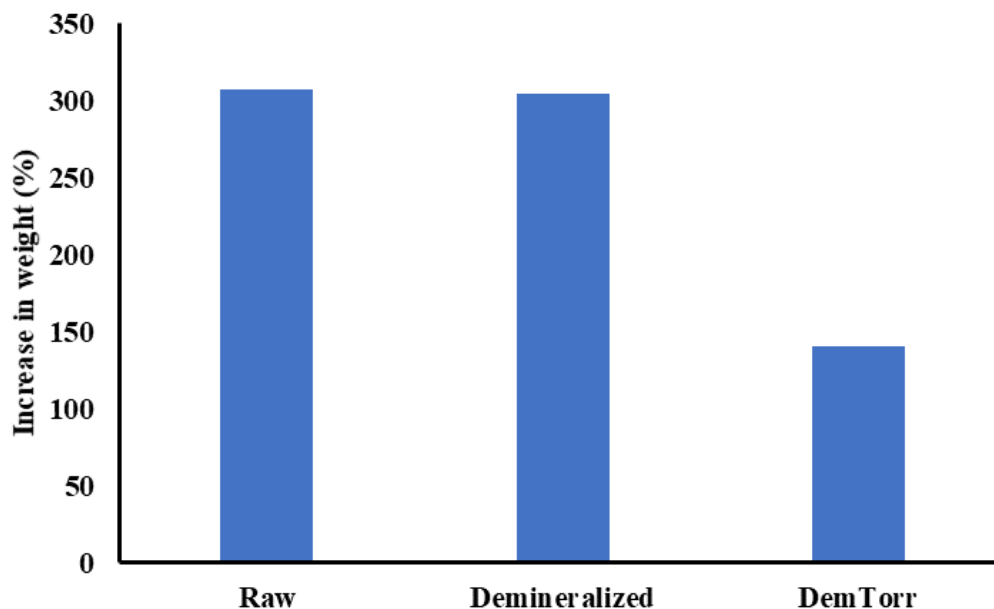


Figure 5.4: Water uptake by raw and treated biomass

5.3.4 FTIR

Every molecule shows a unique spectrum after the absorption of infrared rays based on its natural frequency of vibration. FTIR spectroscopy feats this fact and helps in assessing the structure and structural changes which are caused by the treatment processes in the present study. Figure 5.4 shows the FTIR spectra of raw and treated biomass samples. In native biomass, a strong O–H stretching absorption is seen at 3329 cm^{-1} and a conspicuous C–H stretching absorption at 2907 cm^{-1} can be assigned to aliphatic chain. There are many clear peaks in the fingerprint region between 1750 and 700 cm^{-1} . These peaks can be ascribed as 1731 cm^{-1} for unconjugated C=O in hemicellulose, 1633 cm^{-1} for absorbed O–H and conjugated C–O, 1508 cm^{-1} for aromatic skeletal in lignin, 1455 cm^{-1} and 1423 cm^{-1} for C–H twisting vibrations in lignin and carbohydrates, 1376 cm^{-1} for C–H deformation in hemicellulose and cellulose, 1315 cm^{-1} for C–H vibration in cellulose in syringyl derivatives, 1235 cm^{-1} for syringyl ring and C–O stretch in xylan and lignin, 1039 cm^{-1}

for C–O stretch in hemicellulose and cellulose and 885 cm^{-1} for C–H wagging vibrations in cellulose [110].

In the FTIR spectra of demineralized biomass, the slight reduction in band intensity of O–H can be observed which is caused by the hydrolysis of the carboxylic structure [41]. The band at $2800\text{--}3000\text{ cm}^{-1}$ is attributed to C–H stretching vibration of $-\text{CH}_2$ and $-\text{CH}_3$ functional groups and a minor change in both bands can be observed after acid treatment [87]. A slight change in intensity of bands around 1730 cm^{-1} and 1650 cm^{-1} of the demineralized sample can also be observed which is probably due to the high removal of inorganics comparatively. All above band variations indicate that few changes have occurred in cross linking between different functional groups and thus represents the various acid treatment effects. While in case of demineralized and torrefied biomass residue the peak intensity of O–H band around 3329 cm^{-1} weakens. This variation was resulted from the loss of water and hydrogen bonds resulting from dehydroxylation of hemicellulose and degradation of cellulose [74,111]. In the same spectrum, the change of peak intensity at 2907 cm^{-1} is probably due to decarboxylation reactions in the biomass substrate those are occurred possibly because of degradation in the cellulose and hemicellulose [112–114]. The scission of aliphatic chain may produce CH_4 , C_2H_4 and C_2H_6 in gaseous products. The disappearance of peak at 1338 cm^{-1} and 1302 cm^{-1} can also be observed in Figure 5.4. These peaks show the C–H in plane bending and CH_2 wagging in cellulose. Their disappearance clearly shows that when torrefaction is carried out at $275\text{ }^\circ\text{C}$, it sternly rattled the cellulose following decarboxylation reactions [111]. The spectrum between $1970\text{ to }2030\text{ cm}^{-1}$ shows that the peak becomes prominent which can probably be associated to overtone in the aromatic rings of lignin [113]. Disruption of cellulosic structure is higher at elevated temperatures hence making the overtone noticeable due to prevalence of lignin in the biomass. All the structural changes reported

are the attributes of demineralization and torrefaction processes generated from their acid hydrolysis and deoxidation effects and were conducive to the efficient use of biomass for energy generation.

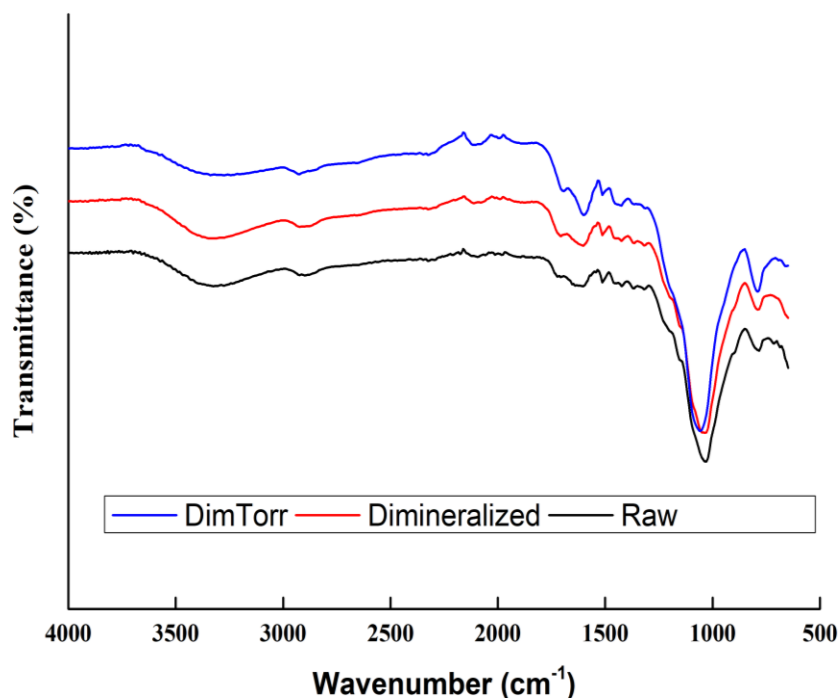


Figure 5.5: FTIR spectrum of raw and treated samples

5.3.5 Thermal degradation study

A study to inspect the thermal degradation of torrefied biomass samples was carried out. The thermogravimetric curves (TG) and derivative thermogravimetric curves (DTG) for the raw and treated samples are presented in the Figure 5.5 and 5.6. In native biomass, three distinct stages of weight loss can be observed which are also recognizable by the peaks in DTG curves. The first stage ($< 200\text{ }^{\circ}\text{C}$) in TG curve is attributed to the moisture loss and light volatile removal and the same change can also be observed in DTG curve. The next stage ($270\text{--}400\text{ }^{\circ}\text{C}$) stems from the thermal degradation of hemicellulose and cellulose. In DTG curve, this stage can be distinguished by a central peak having two shoulders. The first shoulder represents the thermal decomposition of hemicellulose and the second shoulder represents the thermal degradation of the cellulose [116].

The third stage (420-500 °C) shows the degradation of lignin. In case of demineralized biomass, it can be observed that the peaks of treated samples have slightly shifted towards high temperature showing an increase in degradation temperature. This can be explained by the reason that AAEM, which act as catalyst during thermal decomposition, have been removed through acid treatment and cellulose and hemicellulose are now more resistant towards their thermal degradation [101].

In second stage, the decay in weight decreasing profiles of the raw and demineralized biomass samples is sharp and this region is attributable to hemicellulose degradation. A delay in the second stage is observed for the torrefied samples shows the removal of hemicellulose after intense torrefaction. This is because of the dehydroxylation of hemicellulose in the sample which is also consistent with the observation from FTIR spectrum. It may be concluded that during torrefaction, the most reactive segment (hemicelluloses) is affected and demineralization raised the thermal degradation temperature of the cellulose and hemicellulose.

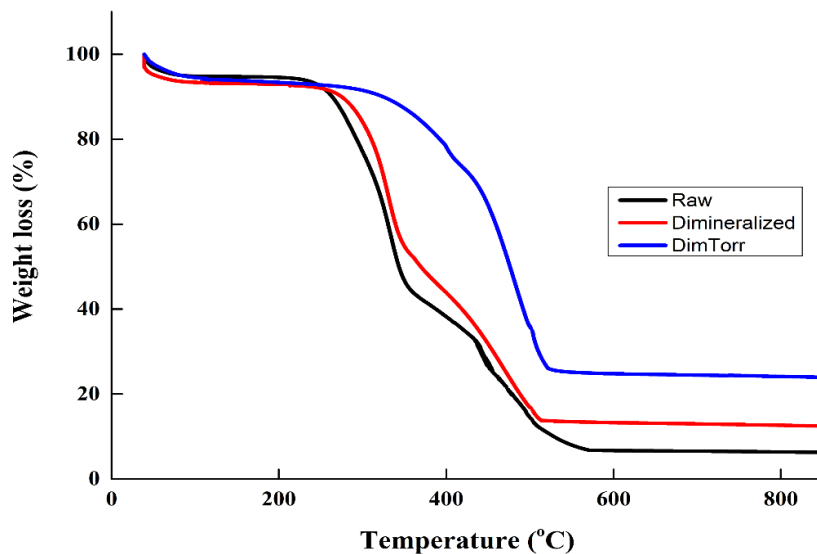


Figure 5.6: Thermogravimetric analysis of raw and treated samples (TGA)

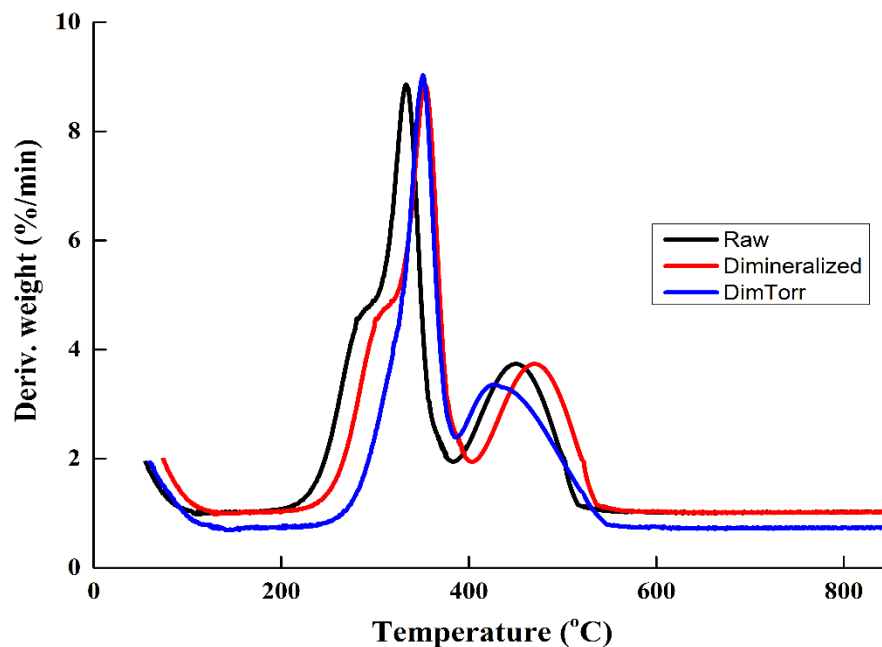


Figure 5.7: Thermogravimetric analysis of raw and treated samples (DTG)

5.4 Conclusion

The agricultural residue can be converted into an efficient fuel after demineralization and torrefaction as thermolyzed samples showed higher carbon contents as compared to its raw counterpart. XRF results showed that leaching biomass with acid at room temperature has the ability to convalesce the quality of biomass for energy generating processes as it reduces the fouling and slagging nature. The reduction of sodium, iron, sulfur, calcium and potassium present a great potential to apply acid leaching process at larger scale. The thermal treatment reduces hydrogen and oxygen contents in biomass because of devolatilization and dehydroxylation of hemicellulose hence bringing it nearer to coal in terms of fuel quality. The higher heating value of demineralized biomass improves upto 4176 cal.g^{-1} . The torrefied samples showed the improvement in calorific value from 3939 cal.g^{-1} to 4356 cal.g^{-1} due to dehydroxylation of hemicellulose thus improving the hydrophobic nature of biomass. On the overall, the treatment

processes not only improved the fuel characteristics of biomass but also made it hydrophobic thus making it an alternative fuel that may be used at commercial level for energy generation.

CHAPTER 6: CONCLUSION

6.1 Conclusion

Biomass residues show a colossal tendency of slag formation and have high oxygen to carbon (O/C) ratio and hydrogen to carbon ratio (H/C) which make them hygroscopic. During combustion, the slag formed reduces the heat transfer rate and causes corrosion of the equipment while hygroscopic nature increases the bulk density and reduces the energy potential and shelf life of the biomass. In this research work, pretreatment processes (demineralization and torrefaction) were performed to reduce the effects of inherent issues of biomass during energy generation.

Demineralization process significantly reduced the ash content of the biomass and increases the heating value. The results showed that leaching performed for 2 hr with H_2SO_4 have removed more AAEM as revealed by the ash content (34.20% decrease) comparatively, however, it has also affected the structure as depicted by SEM and FTIR. The increase of 7.10% in HHV was shown by R6 validating the reciprocal relation between ash content and HHV. The shifting of peaks of treated samples towards high temperature in TG and DTG curves indicated that treated sample are more resistant towards thermal degradation due to the elimination of catalytic role of AAEM.

Torrefaction reduces the H/C and O/C ratios in biomass because of devolatilization and dehydroxylation of hemicellulose. At intense process conditions, more ruination to the structure of thermolyzed samples can be observed which demonstrates the thermal degradation of hemicellulose and evolution of volatile matter as revealed through SEM photomicrographs. The higher heating value of thermolyzed samples improve upto 4913 cal.g^{-1} as compared to raw biomass of 3939 cal.g^{-1} however the mass and energy yield decreases especially at severe torrefaction condition i.e. $300 \text{ }^\circ\text{C}/150 \text{ min}$. The FTIR spectrum showed reduction in the O–H peak

intensity, which can be verified by the reduction in H/C and O/C ratios, due to dehydroxylation of hemicellulose thus improving the hydrophobic nature of biomass. Thermal degradation analysis of torrefied biomass showed three distinct stages of weight loss for all samples. The hemicellulose is the fraction more affected during the torrefaction as observed in the DTG curves.

In order to address slagging and hygroscopic nature of the biomass collectively, the biomass was pretreated with both processes in series. The demineralized and torrefied biomass not only showed the improved hydrophobic nature as water adsorption of the treated biomass reduced by 55% but also reduced the slagging nature as slagging factor of the treated biomass reduced to 0.1 in comparison to the raw biomass having 0.8 slagging factor. The combine treatment also resulted in increased HHV of the biomass i.e. 4356 cal.g⁻¹ in comparison to the raw biomass having 3939 cal.g⁻¹. On the overall, the combine treatment of biomass not only enhanced the fuel characteristics of biomass but also made it hydrophobic thus making it an alternative fuel that may be used at commercial level for energy generation.

6.2 Future work

- A comprehensive study on the optimization of demineralization and torrefaction can be performed to develop proper operating conditions that would produce suitable feedstock for the multiple downstream processes.
- The modeling and simulation study of the combine process could also be performed to observe the one and two-dimensional behavior.
- In future, a thermodynamic analysis could be performed to investigate the equilibrium characteristics of the combine process.
- A life cycle analysis (LCA) of the combine process need to be carried out to evaluate the environmental impacts and the economic benefits.

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