IMPACT OF HYDROFLUORIC (HF) ACID TREATMENT ON MORPHOLOGICAL AND CHEMICAL STRUCTURE OF AGRICULTURAL WASTES

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ABSTRACT

Acid, base and/or water treatments expand biomass utilisation by reducing ash contents and improving energy density and higher heating values. Dilute acid treatment results in negative impacts on the physiochemical structure of biomass. This study aimed to analyse the effects of hydrofluoric (HF) acid (5% w/w) on the morphological and chemical structure of Wheat Straw (WS), Cotton Stalk (CS) and Rice Husk (RH). Scanning Electron Microscopy (SEM) exposed physical changes after treatment, and Fourier Transform Infrared (FTIR) spectroscopy was used to evaluate the changes in available functional groups in the composition of biomass samples. Dilute HF resulted in pronounced changes in morphology and chemical functional groups of all biomasses. Proximate analysis showed carbonaceous material is also affected; the increment in volatiles (9.27%, 7.7% and 6.9% for RH, WS and CS, respectively) and fixed carbon was observed while ash contents reduced. Furthermore, the influence of all samples on the thermal processing of biomass is compared.

Keywords: *biomasses, acidic pretreatment, ash contents, morphology, aromaticity.*

INTRODUCTION

Biomass is a contemporary and complicated biogenic comprising organic–inorganic contents, a solid product that is majorly generated by natural processes. Herbaceous and agricultural biomass is one of the six types. It has an advantage over other types as its use reduces waste [1]. The composition and raw use draw contradiction.

Hemicellulose, cellulose, lignin, ash-forming compounds and some extractives are biomass's main constituents, representing different thermal behaviour during pyrolysis [1]-[2]. The detrital ash-forming compounds are K_2O, CaO, MgO, SiO_2, Al2O3, Fe_2O_3 etc., in biomass feedstock [3]. In previous research, demineralisation with a diluted acid solution (1-7%) has been reported as a suitable method to reduce ash-forming compounds from biomass [4]–[6]. This pretreatment prior to energy generation can improve fuel properties, extensively reduction of energy consumption and save maintenance costs [7]-[8]. The removal of ash-forming compounds is directly related to bio-oil production, which affects the surface morphology, chemical functional groups, and char contents of biomass. In several research, biomass's physiochemical structure was investigatedsing SEM and FTIR spectroscopy analysis [9]-[10]. Also, the acid concentration and strength are important parameters to achieve optimal energy contents and effective removal of ash contents [7],[9]. The previous studies mainly focused on 3% and 7% acidic concentrations. The interesting results are obtained at a higher concentration which strongly affected the surface morphology of biomass investigated by SEM [4]. Moreover, the ash contents were removed at lower concentrations depending on the type of acid [11]. Among acids, HF is a weak acid due to a strong H-F bond but is considered corrosive, which corrodes biomass contents and removes almost all ash contents [3]. The high ash removal and relative increase in the sugar cane bagasse cellulo result in an increase in pyrolysis oil percentage up to 69% [12]. Empty fruit branches and palm mesocarp fibre treated with 2 M HF significantly reduced ash and changed pyrolysis behaviour [3]. HF concentration from 0.5% to 3% increases bio-oil production by up to 13% [12]. Extensive work is conducted to evaluate the acid and biomass efficiency. The impact of dilute HF on morphology and functional groups (including band assignment and deep insight) of wheat straw, cotton stalk and rice husk is scarce. The effects of hydrofluoric acid on surface morphology to change pyrolysis yields are necessary to be evaluated at the micro level.

Biomass energy is one of the main renewable energy sources, and biomass residues offer vast availability for potential energy generation. In previous studies, cereal residues are believed to replicate primary energy due to their larger-scale production. In 2013, food production (670 million metric tons) from cereal crops (wheat and rice) dominated human food supplies [13]. This work aims to modify the previously studied biomasses in Javed et al. [14] and Javed [15]. HF is frequently avoided to enhance biofuel properties due to adverse effects on biomass surface morphology and chemical functionality. This study evaluates the effect of ash removal by dilute HF treatment on three different biomasses' surface morphology and chemical structure. The severity of the effects of hydrofluoric acid at the constant concentration on physiochemical structure analysed by FTIR spectroscopy and SEM

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analysis is compared. Furthermore, the influence of the analysis on the biomass composition (volatile matters, fixed carbon and ash contents) is discussed.

MATERIALS AND METHODOLOGY

Material

Agricultural wastes, Wheat Straw (WS), Cotton Stalk (CS) and Rice Husk (RH) were chosen for this study. Wheat straw (type: AAS11), rice husk (type: Basmati; PK 385) and cotton stalk (type: Bacillus thuringiensis; CIM-598) were collected from HAS Fodder ltd, 140 km North of Lahore, Punjab Rice Mills, Pakhoki and Bulleh Shah Packaging, Kasur, Punjab, Pakistan respectively. Hydrofluoric acid (HF: 38%) was used as received. Another supporting material was distilled water.

Leaching Protocol

The method to carry out the leaching of all biomass samples is shown in Figure 1. The ash-forming compounds (authigenic ash) on the surface of WS, RH and CS samples were removed by washing with distilled water. Prior to acid treatment, all samples were dried in a green gashouse dryer for 48 hours. The selected particle for treatment was 2 mm obtained using a blade mill (Philips; HR2056/00, Pakistan) and sieving. The inverse relation between maximum ash extraction and physiochemical structure was validated using diluted hydrofluoric acid (5% w/w). Approximately 25 grams of biomass samples were separately immersed in dilute acid at room temperature for 2 hours. The ratio 1/15 (1 g solid residue/ 15 ml diluted acid) showed the complete immersion of all samples separately into an acidic solution. The whole process was employed with shaking using Orbital Shaker at 250 rpm to enhance the leaching efficiency. The treated WS, RH and CS samples were filtered and washed with distilled water to maintain a constant pH value of 7. The experimental procedure was repeated three times separately for each sample. All acid-treated samples were oven dried at 105˚C for 24 hours and air-tightened in plastic (Poly propylene; PP) bags.

Figure 1 Leaching process

Methodology

The fixed carbon, moisture contents, volatile matter and ash contents were calculated using proximate analysis. The volatiles in biomass samples was measured according to ASTM standard method D3174, and moisture contents were calculated using ASTM D3173 and ash contents by D3175 for biomasses. Then, fixed carbon in all samples was calculated using the following equation.

$$\%\ Fixed\ carbon = 100 - (Volatiles + Moisture + Ash)$$

SEM micrographs of all biomass samples were taken using JEOL JSM-6480 LV. The morphology was evaluated at low vacuum and 15 kV acceleration voltage. All samples were analysed without conductive coating. The samples were mounted on double-sided carbon tape on a metallic stab.

FTIR (Agilent Technology 630) spectrometer was used to evaluate changes in surface functional groups available in all samples. All samples were grounded and analysed using Attenuated Total Reflection (ATR) method without a binding material. The spectral resolution was 16 cm^{-1}, and the IR region ranged from 4000 to 650 cm^{-1}.

RESULTS AND DISCUSSION

Proximate Analysis

The acidic treatment of biomass samples has shown great changes in volatile, fixed carbon and ash contents, as given in Table 1. All samples experienced a decrease in ash contents compared to raw samples, which agrees with the literature [16]. The leaching efficiency of HF is high compared to other strong acids [15]. The leaching efficiency of the leaching process is calculated as a percent reduction in ash contents.

HF-RH has the highest deashing efficiency (77.4%) due to comparatively higher amounts of metals. HF removed 76.1% and 72.9% of total ash from WS and CS samples, respectively. The efficiency depends on the type of biomass. The RH sample has the highest ash contents and showed the highest removal efficiency. The effective capacity of dilute HF to dissolve carbonates may depend on the inorganic and the amount present in biomass. The metal oxide hydrolysis and dissolution are possibly hindered due to reduced breakage of lignin and hemicellulose electrostatic interactions. The FTIR showed a slight decrease in bands related to hemicellulose, indicating its removal. Also, it can be verified from the SEM analysis.

The improvement in the volatile matter and fixed carbon after acid treatment is a normal phenomenon [6],[16]-[17]. Removing inorganic compounds from biomass comparatively increases the overall cellulose, hemicellulose and lignin composition while these components are also subsequently reduced. The carbonous matter remains in higher amounts even after its dissolution in acid. HF-treated RH and WS have the highest Volatile Matter (VM), resulting in 9.27% and 7.7% increment, while HF-CS has shown the lowest increase in VM (6.9%) after acid treatment. CS proved to be more reluctant regarding ash exploitation than WS and RH. Comparatively, HF-RH shows more damage in chemical functional groups and SEM images. The reduction in moisture contents is related to drying after diluting HF treatment.

Table 1 Proximate analysis (MC: moisture contents, VM: volatile matters, FC: fixed carbons & AC: ash contents)

Sample ID	MC (%)	VM (%)	FC (%)	AC (%)	Ref.
Raw-WS	7	69.19	14.06	9.75	[15]
HF-WS	5.8	74.57	17.3	2.33	
Raw-CS	7.2	60.3	25.84	6.66	[14]
HF-CS	4.91	64.47	28.82	1.8	
Raw-RH	7.2	65.9	12.83	14.07	[14]
HF-RH	5.95	72.01	18.86	3.18	

Morphological Characteristics

The surface morphology of the samples was analysed using Scanning Electron Microscope (SEM) to observe the changes induced by HF treatment. The SEM images of all samples are shown in Figures 2, 3 and 4.

The SEM micrographs of the cotton stalk are presented in Figure 2. Raw-CS has bulky fibrous material on the main structure, making the surface uneven. The small particles are agglomerated to make a greater particle with pores on the surface and a lumpy surface on the main structure (epidermis). The dilute acid treatment has changed the surface morphology of the sample. The fibrous layer disappears due to the dissolution of organic material. Dilute HF corroded the surface while the main framework was eroded. The changes in the main framework show the effect of HF on the sample's chemical structure. The upper layer is completely damaged, and some of the remaining parts show the pertained hemicellulose close to the outer layer of cellulose. In some cases, cellulose is also scarce, which shows the washing out of carbonaceous materials of biomass. These changes in morphology can be verified by changes in chemical functional groups available on biomass surfaces, as shown in Figure 2.

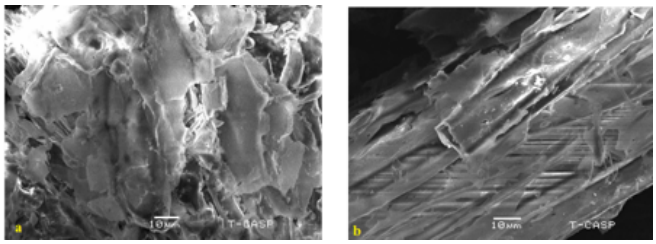

Figure 2 SEM images a) Raw-CS b) HF-CS

The SEM images of WS samples are presented in Figure 3. In Raw-WS, a thin glassy layer of carbonaceous material is attached to the main structure. The glassy layer appears in an irregular prototype, possibly because of the mechanical process (harvesting). In HF-WS, the layer is removed, and a small part of the thin layer is fused to the main structure due to the corrosion of the WS sample. The main framework is uncovered, and an increase in the roughness of the surface can be observed. Also, HF created interspaces where the thin layer was not present. In some particles, the surface has become plain, and the spots on the surface show corrosion to damage the main structure of the sample.

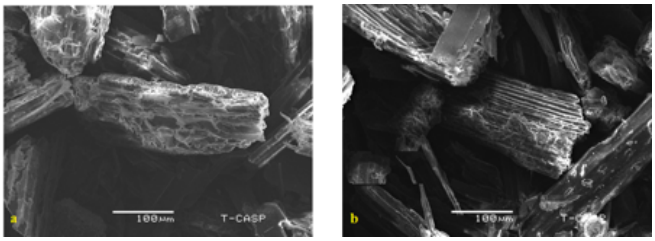

Figure 3 SEM images a) Raw-WS b) HF-WS

The SEM images of rice husks are shown in Figure 4. The surface of Raw-WS has many layers of fibrous material on the main framework. The lumps of organic matter appeared in an irregular pattern making a rough surface. The small particles of fibrous material are sticky and dispersed on the surface. The epidermis of Raw-RH is covered by cuticle-covering pores (stomata) on the main structure (epidermis). The diluted acid treatment washed the upper layers, which uncovered the number of pores available on a structure. The stomata in Raw-RH are unclear, and some are very small as compared to HF-RH. The wide openings in HF-RH are clearly indicating the adversity of the sample. The stomata are usually available in fewer numbers on biomass surfaces. After HF treatment, the sample is eroded, and interspaces are created. The pores are enlarged due to the corrosion of the samples.

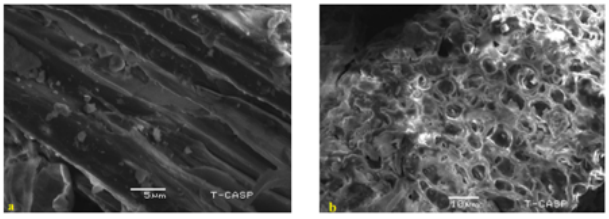

Figure 4 SEM images a) Raw-RH b) HF-RH

Aromaticity Assessment

The chemical structure of the three different biomass samples is studied using infrared spectroscopy. FTIR technique was employed in this investigation to study the effects of HF's corrosive nature on the biomasses' surface chemical structure. Figures 5, 6 and 7 represent the FTIR spectra of raw and pretreated biomass samples. For the spectra of Raw-WS and Raw RH, the CS are taken from [15] and [14], respectively.

In the IR region of all samples, the first band between 3700-3000 cm^{-1} shows alcoholic, phenolic and carboxylic functional groups resulting from stretching vibration of O-H [10]. The strong band became less intense for WS and more intense for RH and CS. The variation may be attributed to varying contents of biomass. The stretching vibrations of O-H show the hydrophilic tendency of fibre. The second band between 2800 cm^{-1} and 3000 cm^{-1} has two clear shoulders at the left (2915 cm^{-1}) and right (2847 cm^{-1}) of the band at the peak intensity of all raw samples. In literature, this band is associated with stretching vibration of $-CH_2$ and $-CH_3$ functional groups. The left shoulder with an absorption peak at 2915 cm^{-1} is assigned to C-H stretching [18]. After treatment, the shoulders are completely wiped out from the IR region.

The third band at 2200-2000 cm^{-1} show different intensity for each raw sample. Raw-RH depicts the lowest intensity in this band, while Raw-CS shows the highest intensity, followed by Raw-WS. After acid treatment, the band intensity changed for all samples. The band intensity slightly increased for HF-RH and HF-CS, while HF-WS decreased per se.

The band around 1730 cm^{-1} is assigned to the free carbonyl group due to the stretching vibration of C=O (hemicellulose). The small peaks at 890 cm^{-1} and 1159 cm^{-1} are due to C-H deformation and C-O-C stretching (hemicelluloses and cellulose) [19]. Both peaks have become sharp in acid-treated samples while band (1730 cm^{-1}) intensity slightly increased for HF-CS and HF-RH. The band around 1185 cm^{-1} is related to syringyl units of lignin. The absence of this band in HF-RH confirms the removal of lignin contents from the sample.

The attached band at 1510-1650 cm^{-1} shows the presence of aromatic groups pertaining to C=C stretching vibration [10]. All raw samples show different band intensities according to the presence of aromatic rings (lignin and carbonate inorganics). The band intensity of Raw-CS is the highest, while Raw-RH has the lowest, followed by Raw-WS. After HF treatment, the band intensity showed a maximum decrease for HF-CS and HF-WS and the lowest decrease for HF-RH. The joint vibration of lignin and carbonate inorganics is disturbed, and the lignin is nearly deprived of inorganics. The maximum decrease in intensity shows the higher removal of inorganic contents. This band is also affected by the acidity of the leaching agent. Higher acidity reduces the band intensity [10],[15]. The different vibration modes between 1400 and 650 cm^{-1} exist. In literature, the complication of this region is reduced due to the detection of vibrations related to some specific units, such as lignin. The spectra of different samples indicated the characteristic vibration of the lignin unit at 1240 cm^{-1} (C=O stretching) and 850–750 cm^{-1} (C-H bending) [20]-[21]. Among different biomass samples, CS pretreated by HF showed more considerable changes in these bands' intensity than HF-RH and HF-WS. The clarity of the band for HF-CS is attributed to ash content removal, which can be verified in Table 1 as HF-CS has shown changes in all bands' intensity related to inorganics. In contrast, the cellulose and hemicellulose transmission reveals several bands between 1440 and 1400 cm^{-1} resulting from O-H bending. A slight change in bands' intensity in this region could be observed for treated samples.

The strongest broadband at 1030 cm^{-1} is usually observed for all biomass types. This band results from high cellulose and hemicellulose (C-C/ C-O stretching vibration) [15]. The ash removal and intensity variation classify the nature of the effect on cellulose and hemicellulose. The band intensity decrease shows the damage of biomass constituents, while peak sharpening is related to high inorganic removal. The acid treatment usually makes this band intense and sharp, depending on the acid type. The inorganic acids, except for sulphuric acid, increase band intensity, possibly due to the diprotic effect [15]. In all figures of IR spectra, the treated samples illustrate the effect of the corrosive nature of HF by reducing band intensity significantly. The decrease in band intensity shows the adverse impact on the chemical functionality of all biomass samples, mainly depending on its composition. The maximum decrease was observed in HF-WS, followed by HF-RH, while HF-CS experienced less decrease. This may be attributed to variations in the inorganic oxide concentration of CS, WS and RH. The plant is similar if the overall inorganic concentration of cotton stalk is compared with cotton husk. Cotton husk has a higher amount of CaO (20.95%), K_2O (50.02) and MgO (7.59%) as compared to WS and RH (CaO (8.21% & 2.46%), K_2O (24.89% & 12.59%) and MgO (2.74% & 2.71%) respectively). The percentages are compared in the literature [1]. Consequently, CS provides more metal oxide to react with acid, due to which the chemical functional group damage is controlled.

The change in physiochemical structure mainly depends on biomass and acid type. The ash reduction efficiency participates in structural changes due to different types of ash-forming constituents present in biomass. HF-RH has shown significant changes in chemical and physical structure due to its ash-forming constituents. The chemical structure was possibly damaged due to the removal of carbonaceous material, as shown by SEM micrographs. The outer layers after treatment are absent, and possibly the inner layers are at risk. In the IR spectra of all samples, the peaks are sharpened due to the removal of inorganic contents. Removing inorganics from carbonates may disturb the chemical functional groups depending on the removal efficiency, biomass type and type of acid.

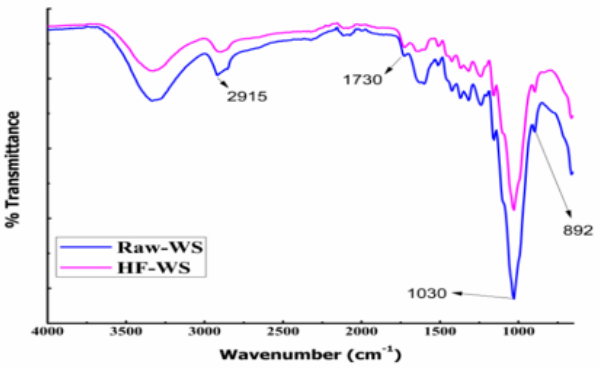

Figure 5 FTIR spectra of WS; Raw-WS [15]

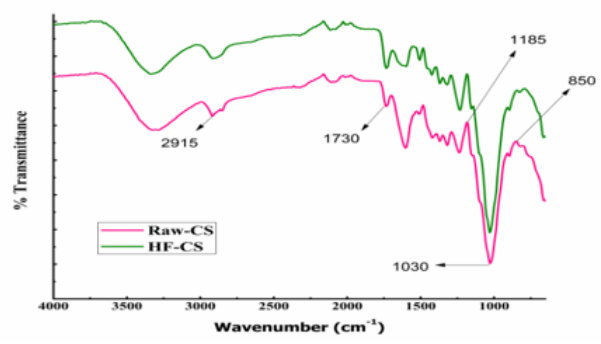

Figure 6 FTIR spectra of CS; RAW-CS [17]

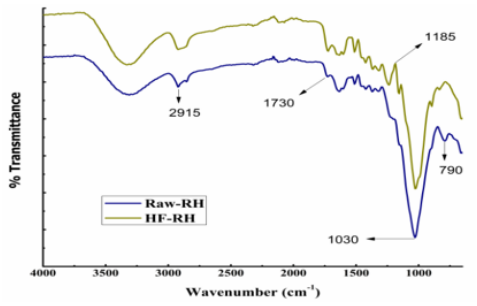

Figure 7 FTIR spectra of RH; Raw-RH [17]

Influence of Morphological and Chemical Structure on Pyrolysis

Biomass composition varies depending on the type of biomass. Typically, the inorganic and organic contents (carbohydrates) are the main components. The ash contents could vary from 1% to 15% [14]. The ash contents mainly result from AAEMs available as oxide, oxalate, chloride and carbonates in all types of biomass. The other part comprises cellulose, hemicellulose and lignin [2]. The lignin and hemicellulose are linked through electrostatic interaction in carboxyl and hydroxyl groups. Acids have a high tendency to react with metals pertaining to the inorganic part of biomass [17]. The chemical linkage of inorganic (carbonate) and organic (lignin) parts cause joint vibration. This linkage is risked when dilute acid reacts with ash-forming components (metals) such as K, Si, Mg, Ca and Na. Also, acids like HF are corrosive enough to dissolve organic matter causing changes in organic composition. The organic matter forms volatile matter at a temperature from 250 to 500, and fixed carbon (above 500) followed by ash contents (after complete burning).

FTIR spectroscopy is another technique to confirm the changes in volatile matters available in biomass samples. The higher O-H, C=O and C-O-C intensities indicate a larger portion of volatile matters, which agrees with proximate analysis [4]. The changes in the FTIR bands confirm the compositional variation of all biomass samples.

The physical surface of samples also affects the heating phenomenon, which can be explained on the following ground. SEM images of RH-treated samples reveal the surface has become rougher as compared to the raw sample. The appearance of cavities in treated samples also increases the char contents during pyrolysis and decreases the volatile matter by reducing the condensation reaction. The volatile matters condensed in the void spaces present on the surface of the sample. In the case of HF-RH samples, the surface becomes rougher, and large pores are generated, which could cause an increase in porosity. The increased porosity could reduce the volatile matter due to vapour condensation [22].

Generally, acids dissolve first hemicelluloses, then cellulose and have fewer effects on lignin [22]. The treated samples showed more changes in cellulose and hemicellulose contents than lignin contents. The most obvious decline of hemicellulose in all samples can be observed by changes in the chemical bonding of C=O (FTIR spectra). The reduction in hemicellulose in all treated samples and lignin in HF-RH could produce better results in the case of bio-oil production. Lignin and hemicellulose contribute to maximum char production during biomass pyrolysis, resulting in loss of product yields (gas and/ or bio-oil).

CONCLUSION

In this work, the inverse impacts of dilute hydrofluoric acid treatment on the physical structure and surface functional groups of cotton stalk, wheat straw and rice husk are studied simultaneously. The morphological and chemical structural alteration is mainly subject to the type of ash-forming compounds in all samples. The bands' thorough study assisted in analysing the HF treatment effects on volatile matters, fixed carbons and ash contents. The increased volatile and fixed carbon contents showed a reduction in ash contents and related bands' intensity in the IR region for all biomass samples. Rice husk showed significant changes in physiochemical structure. The reduction in band intensity is directly related to the oxygenated carbon and lignin attached to carbonates. After HF treatment, the maximum ash reduction of 77% and the highest volatile content of 9.27% were observed in rice husks. In the IR region, the bands for hemicellulose and lignin experienced the most obvious decline, which may produce fewer char contents in the thermochemical processing of biomass. Dilute HF-treated wheat straw, rice husk and cotton stalk could increase the bio-oil yield in pyrolysis due to reduced ash contents.

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