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Physiochemical and Thermal Analysis of Diverse Leaching Reagents by Demineralising Raw Wheat Straw for Clean Energy Production: TGA-FTIR

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The increased consciousness in greenhouse emissions has encouraged the expansion of new technologies to accommodate the internment and appropriation of carbon dioxide. Demineralisation handling by leaching consuming different reagents, including hydrochloric acid, nitric acid, as well as sodium hydroxide, were considered intended for ash reduction and their effects on the physical, chemical, and thermal behaviour of wheat straw. Dilute-acid reagents reduced the maximum ash content in biomass as 92.94 % in the case of 0.6 mol of HCl, followed by 0.4 mol of HNO_3 having 90.75 % ash reduction. While in the case of basic reagent, 0.2 mol of NaOH reduced 85.73 % ash having lower value than the acidic reagents. The acidic leached samples show higher heating value than the basic one as the calorific value is increased by more than 4.15 % and decreased by 3.95 %. It is because the basic reagents rescind the assembly of the hydrocarbon, as portrayed through SEM and FTIR spectra.

1. Introduction

Biomasses are considered as a significant renewable auxiliary energy reserve. Oil and gas produced by the biomass, can be used as substitutes for oil or gas. Several biomass resources, such as agricultural, forestry, municipal, and industrial wastes (Mortari et al., 2010), can be used as fuel (Wilson et al., 2011) for power generation. Biomass collected from wheat crops usually contains a high concentration of ash, which is more than 6 % (Aziz, 2019). The thermo-chemical changes of biomass containing a high quantity of ash enforces a harmful impact on apparatus (Chen et al., 2014), conversion efficiency (Chin et al., 2015), and the superiority of fuel crops (Wang et al., 2015). It also comprises some inorganic components like alkali and alkaline earth metals (AAEM) holding Mg, Ca, Na, and Fe. AAEM is the primary contributor to the inorganic portion of biomass fluctuating from 1 - 15 % dependent on the type of biomass. When combustion temperature moves higher than the ash melting point, then it melts down and sticks to the burner's surface, making a shielding layer (Aslam et al., 2016), which results in reduced thermal efficiency.

Wheat crop is among the top five crops of Pakistan and occupies 41 % cultivated area (Saeed et al., 2015). Wheat straw is residual after removing wheat grains. Pakistan produces 18.63 Mt of wheat residue per annum (Siddiqi et al., 2018). Demineralisation pre-treatment by physical and chemical means, such as fractionation, centrifugation, and leaching, as well as multi-step procedures to eliminate the ash-forming residents in biomass (Yu et al., 2014), have been covered in (Wigley et al., 2015). Numerous leaching reagents have been remarked for the demineralisation of biomass (Eom et al., 2011). Lignocellulosic biomass comprises elements which are insoluble in water, also can only be detached by acidic reagents (Scott et al., 2001). Segments of hydrocarbons, existing in biomass, may also dissolve in extractive reagents throughout the abstraction of minerals. Demineralisation causes undesirable loss or decay of organic substances from biomass, that decreasing the worth of the residual biomass for energy applications (Hong and Wang, 2009).

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The main concern of this study is to reduce the effect of minerals and ash related problems in combustion process because all fuels have ash contents. Due to the inorganic components existing in the ash, demineralisation of wheat straw by diverse leaching agents was performed to investigate its thermal and physiochemical properties, subsequently leaching treatments to associate its alteration with raw and leached wheat straw. Also, chemical and physical structure have been studied using Fourier-Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopes (SEM), to analyse this consequence after mineral extraction (Lv et al., 2010).

2. Methodology

2.1 Materials and Methods

Wheat straw is collected from rural areas of Sahiwal district, Punjab, Pakistan. Primarily, samples were pallid by distilled water to eliminate dust particles, later drying, its size is reduced to 3.25 mm particle size with ASTM sieve number 6. The leaching reagents used in this study were sodium hydroxide (NaOH), nitric acid (HNO_3-70 %), and hydrochloric acid (HCl-37 %) having concentrations of 0.2, 0.4, and 0.6 mol for each reagent, respectively. TGA with model specifications (SDT Q600) tests were made to observe the thermal degradation performance of the samples under ASTM E1131 standard. A platinum crucible, occupied with 12 mg sample, was heated evenly to 500 ºC in the nitrogen atmosphere. Then the temperature was increased from 500 to 950 ºC, in the oxygen atmosphere, for complete combustion. The temperature was amplified at a rate of 10 ºC per minute throughout the whole procedure. Ash was found through the insertion of the dried sample in a muffle furnace for 5 hours at 575 ºC as established by the ASTM Standard E-1755-01. Ash percentage is calculated by dividing the resulted ash to the initial weight (before combustion) of the sample, and percentage ash reduction can also be obtained. Elemental analysis was performed to study the leaching effects on basic elemental composition, including nitrogen, sulphur, hydrogen, carbon, and oxygen contents on dry wt. % basis, using CHN-628 analyser by LECO Corporation under ASTM standard D-5291. Heating values for the treated samples were evaluated by using the LECO AC-500 bomb calorimeter under ASTM standard D-5865-13.

Fourier transform infrared with model specifications (FTIR-Cary 630) spectroscopy tests were conducted under ASTM standard E-1252, to study the chemical structural variations in wheat straw after demineralisation. SEM with model specifications (Quanta 250, FEI) tests were completed, under low vacuum at 5 kV accelerating voltage, to detect the surface morphology of wheat straw after demineralisation. The gold coating was applied to samples as a conductive layer to perform the tests.

2.2 Sample Formation

12 g conditioned wheat straw was well shaken with each reagent in a conical flask occupied with 250 ml of distilled water at room temperature (25 - 27 ºC). Samples were positioned on an orbital shaker for 2 hours at 250 rpm for the maximum interaction between biomass and leaching reagents. Later, acidic, and basic preserved samples were washed out with distilled water until the samples demonstrated neutral pH. Then those neutralised leached samples were positioned in the dehumidifier for 24 h at 105 ºC to eradicate moisture contents from the prepared samples. Table 1 has the samples ID’s prepared through leaching methodology.

3. Results and Discussions

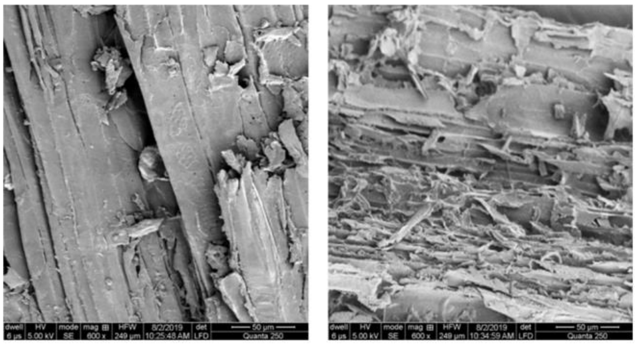
3.1 Demineralisation effect on ash contents and calorific value

The comprehensive ash analysis is given in Table 2. The sample C_3 shows the highest ash reduction up to 92.94 % among all samples used in this study. In the case of HNO_3 treated samples, sample H_2 demonstrates higher ash reduction up to 90.75 %, and for NaOH treated samples, sample N_1 has the highest ash reduction up to 85.75 %. Further analysis was performed on sample C_3 of reagent HCl, sample H_2 of reagent HNO_3, sample N_1 of reagent NaOH and sample R of raw Wheat Straw.

Biomass contains organic matters whose essential elements are hydrogen and carbon. The wt. % ratio of C/H describes the number of hydrocarbons (Jiang et al., 2013). Table 3 demonstrated that the C/H ratio had slight fluctuations for raw material as well as leached samples. We perceived an important reduction in the C/H ratio of basic treated samples inspecting the high subtraction of organic content in sample N_1. On the other hand, the samples which were treated with acid showed additional calorific value as the heating value of sample C_3 was amplified by 4.15 % and sample H_2 expressed 3.74 % increment in calorific value as compared to the sample leached with basic agents. In the case of sample N_1, a 3.95 % reduction in heating value was noticed. This decrement in heating value was due to the hydrocarbons dissolution caused by sodium hydroxide (NaOH) during demineralisation.

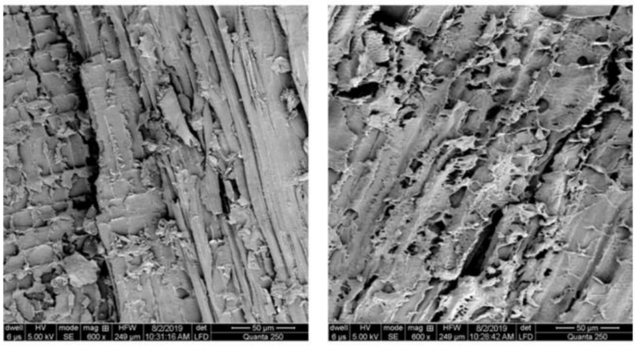
3.2 Demineralisation effect on physical and chemical structure

The surface analysis of all treated samples (C_3, H_2, N_1) and raw wheat straw (R) are shown in Figure 2. Raw Sample has a smooth surface as compared to the other samples; sample C_3 has asymmetrical and spongy structural destruction followed by sample H_2, which has difficult surface destruction due to the acidic reagents. Sample N_1 depicts corrosion, fouling, fluffiness, and porous surface structure, as shown in Figure 2.



a Sample R (Raw)

b Sample C_3 (0.6M HCL)



c Sample H_2 (0.4M HNO_3)

d Sample N_1 (0.2M NaOH)

Figure 2: Surface morphology (a) Raw (b) 0.6M HCl (c) 0.4M HNO_3 (d) 0.2M NaOH

Table 1: Samples of Identification for selection

Sample ID	Reagent Type	Concentration Mole
R	Raw Material	N/A
C_1	HCl	0.2
C_2	HCl	0.4
C_3	HCl	0.6
H_1	HNO_3	0.2
H_2	HNO_3	0.4
H_3	HNO_3	0.6
N_1	NaOH	0.2
N_2	NaOH	0.4
N_3	NaOH	0.6

Demineralisation by leaching reagents causes mineral elimination and dissolution of hydrocarbons because of the leached biomass has a porous surface and structural damage (Yu et al., 2009). According to the consequences found, it is realised that the samples treated with the acidic reagents had more surface variations relative to NaOH leached samples from FTIR. Because leaching with basic reagents (NaOH) demonstrated additional devastation of hydrocarbons, these fluctuations can be realised from the SEM and FTIR spectra of sample N_1. The FTIR spectra were observed to inspect the chemical variations and occurrence of diverse functional groups in common raw and leached samples. The evaluation of FTIR spectra for the samples (C_3, H_2, N_1, and R) are shown in Figure 3. The peaks among 2,850 to 3,550 cm^{-1}, show that there was a precise intermolecular stretched and bonded alcoholic structure of alcohol and (O - H) (Asadieraghi and Daud, 2014). The peaks between 2,850 to 3,100 cm^{-1}, illustrate that there were lignin structure having aliphatic (-CH2) methylene groups and carboxylic acid (Aslam et al., 2016). The peaks for the sample N_1 show less lignin as compared with other leached samples.

Table 2: Demineralisation Effect on ash removal concerning raw sample

Sample ID	Ash Contents %	Ash Content Reduction %
R	6.38	N/A
C_1	0.63	90.12
C_2	0.51	92
C_3	0.45	92.94
H_1	0.65	89.81
H_2	0.59	90.75
H_3	0.69	89.18
N_1	0.91	85.73
N_2	1.25	80.4
N_3	1.84	71.15

Table 3: Ultimate & Proximate analysis of raw and demineralised samples

Sample ID	Carbon Content C (%)	Hydrogen Content H (%)	Nitrogen Content N (%)	Sulphur Content S (%)	Oxygen Content O (%)	Calorific Value kcal/kg	% Change in Calorific value	C/H Wt. %
R	43.95	5.92	0.73	0.11	49.29	4,274.22	N/A	7.42
C_3	42.56	5.87	0.69	0.09	50.79	4,451.60	3.98	7.25
H_2	41.25	5.79	0.7	0.07	52.19	4,434.06	3.60	7.12
N_1	38.41	6.30	0.71	0.10	54.48	4,105.09	-4.12	6.10

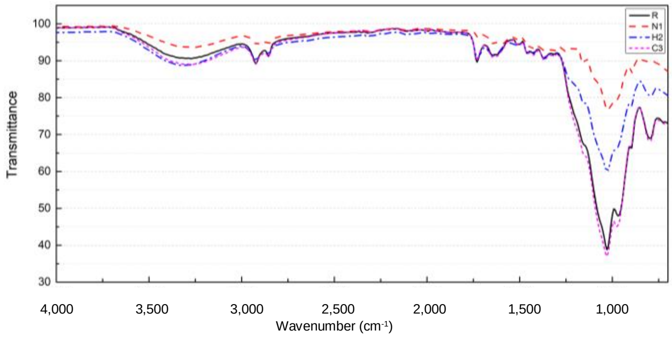


Figure 3: FTIR spectra of raw and acidic and basic demineralised samples

The peaks in the interval 1,650 to 1,800 cm^{-1} having weak (C - H) bonding present in aromatic compound usually overtone type. Anhydride derivatives of hemicellulose and the peak for sample N_1 have been condensed in this range. This shows that the basic leached sample dissolves the hemicellulose structure of wheat straw. It was observed in the limit of 1,605 to 1,635 cm^{-1} the medium giving the vibrations of the C = C bond of conjugated alkene of lignin content had been found. In the range of 950 to 1,050 cm^{-1}, it was observed a high elimination of minerals for the HCl acidic leached sample C_3 as compared to raw and base treated samples, but the chemical assembly had been damaged more in NaOH as it affects the chemical structure more than acidic reagents.

3.3 Demineralisation effect on thermal degradation

Thermogravimetric analysis (TGA) demonstrated the thermal degradation behaviour of diverse wheat straw samples. Figure 4 demonstrated the TGA curves for samples C_3, H_2, N_1, and R. There were four regions on each curve, which can easily be recognised. The first region between 0-105 ºC shows the subtraction of moisture contents, and the second region between 250 - 400 ºC specifies the degradation of the volatile matters. The third region between 450 - 650 ºC and the fourth region between 650-900 ºC were related to carbon degradation and ash production. In the first region, the dehydration of the biomass and decomposition of the small volatile contents was observed. With the temperature range of 250 - 400 ºC, there are two-stage functions one is from 250 - 350 ºC in which the biomass had rapid degradation due to the decay of unbalanced hemicellulose components and the second one is in the range from 350 ºC to 400 ºC related to cellulose thermal breakdown. The lignin content decomposition can be detected in the third region. In the last region, there was a continuous straight line observed for all the samples because of the ash left after complete combustion of the biomass.

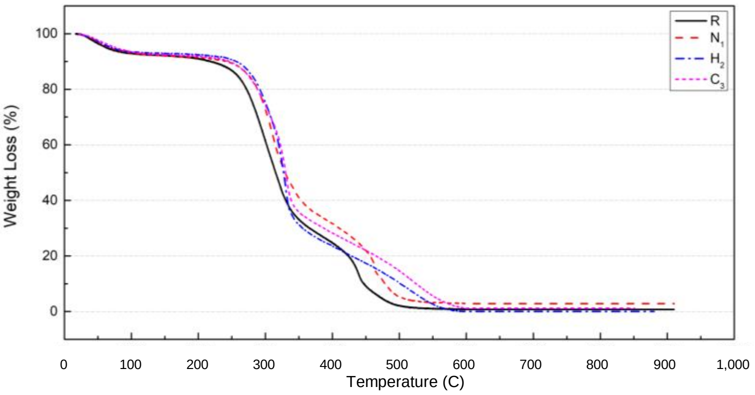


Figure 4: TGA curves of raw and acidic and basic demineralised sample

It was observed that the leached samples showed thermal degradation at higher temperatures as compared to the untreated (Raw) sample because of the inorganic content reduction. This is because the inorganic matter works as a catalyst in raw biomass as these minerals cause decomposition of biomass at a lower temperature. It was established that AAEMs, support the material for thermal degradation at low temperature, and after treatments, thermal degradation temperature increased due to a reduction in the quantity of AAEMs.

The inception of the thermal treatment of the sample resources were synchronised through data provided by (Siddiqi et al., 2018) who considered the thermal analysis (Phasee and Areeprasert, 2017) as well as de-volatilisation. Grain sizes less than 4 mm and model size about 12 g of each configuration under nitrogen till 500 ºC and oxy-fuel atmospheres after 500 ºC at the rate of heating 10 ºC/min were used. The activation energies in oxygen and nitrogen (Mehdi and Siddiqi, 2019) remained in the identical series (approx.) of that calculated in this research for the different materials through the virtually same size of the particle, temperature conditions, and rate of heating (Muthuraman et al., 2010).

4. Conclusion

The significance of this study is the use of wheat straw as fuel at the industrial level after treatment. After demineralisation of a given sample, the acidic leached sample has proven to be the most effective reagents concerning basic samples as it reduces the ash contents to its maximum level, which is the leading cause of slagging and fouling. It is found that the samples treated with acidic agents show more thermal stability than basic reagents. There is a massive increase in the calorific value of the acidic leached samples. Combustion analysis indicated that the thermal stability was found to be increased after demineralisation. The lowest quantity of minerals in the sample causes extra stability for energy compliance. The increase in the decay rate and time through the demineralisation caused high reactivity and produced extra productive energy. This reactivity is beneficial is there is a need to obtain additional energy in a small interval of time. There is way to utilise local waste as a fuel to generate energy with low emissions and ash.

Increase the labour cost for treatment of the fuel, is the major limitation of this work. In future research, this limitation will also be under consideration.

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