



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

IJIRSET

International Journal of Innovative Research in
SCIENCE | ENGINEERING | TECHNOLOGY



INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 11, Issue 7, July 2022

ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA

Impact Factor: 8.118



9940 572 462



6381 907 438



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Investigation on Hydrophobicity of Raw and Torrefied Gram Stalk

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ABSTRACT: Torrefaction improves the thermochemical properties of biomass that are relevant to combustion, co-combustion with coal, or gasification. This study examines torrefaction of gram stalk and hydrophobic properties of the raw and torrefied biomass. Three different temperatures were used for torrefaction i.e., 200°C, 250°C and 280°C for 10 min duration. Product evaluation and mass and energy losses during torrefaction were measured. Similar to other work, torrefied biomass characterized by a more brownish colour. The torrefaction process reduces the swelling tendency of the biomass in water from initial value of 344.46% to 138.07% only for 24 hrs.

KEYWORDS: Hydrophobicity Characteristics, Torrefaction, Gram stalk, Mass yield and Energy yield.

I INTRODUCTION

Biomass has always been an important energy source for the country. It is renewable, widely available, carbon-neutral, and has the potential to generate significant rural employment. Biomass energy can be used to generate heat and electricity in modern devices ranging from very small-scale domestic boilers to multi-megawatt size power plants electricity (e.g., via gas turbines), or liquid fuels for motor vehicles such as ethanol or other alcohol fuels. Biomass, as a high moisture fuel, requires a significant amount of energy to dry. Furthermore, due to its hygroscopic (water-absorbing) nature, dried biomass absorbs moisture after being stored for a period of time. As a result, for industrial use, biomass must be hydrophobic (water repellent) rather than hygroscopic in nature. Torrefaction is a process that can help overcome some of the above limitations of biomass. Torrefaction is an inert-atmosphere thermal treatment that improves the thermochemical properties of biomass, making it more suitable for energy generation. This process removes moisture and carbon dioxide while also depolymerizing the long polysaccharide chains, resulting in a hydrophobic solid with a higher energy density (on a mass basis). Biomass power and bagasse cogeneration are major alternative uses for non-fodder and non-fertilizer agricultural residues. The Ministry of New and Renewable Energy in India (MNRE) implemented the Biomass Power/Cogeneration programme with the primary goal of promoting technologies for making the best use of the country's biomass resources for generating grid power. This study reports results on hydrophobic behaviour of raw and torrefied gram stalk and provides base regarding storage and power generation from biomass.

II. RELATED WORK

Pimchuai *et al.* (2010) The torrefaction of rice husks and four additional agricultural waste products (sawdust, peanut husks, bagasse, and water hyacinth) in nitrogen is studied in this work. Temperature and residence time for the process, were regulated in the range of 250–300°C and 1-2 h, respectively. It is observed that a specimen torrefied at a higher operating temperature result in a lower moisture absorption. The rise in the moisture content of the torrefied sawdust was 2.16% compared to 150.33% for raw sawdust. The maximum rise in the moisture content is 17.71% for the torrefied water hyacinth, while it is 197.54% for raw water hyacinth. Acharjee *et al.* (2011) studied the effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. Raw lignocellulosic biomass and four samples that had undergone thermal pretreatment were both assessed for their equilibrium

moisture content (EMC) at relative humidity levels ranging from 11% to 97% at a constant temperature of 30°C. Wet torrefaction was used to prepare three samples, which were treated in hot compressed water at 200, 230, and 260°C. A second sample was created using dry torrefaction at 300°C. Raw biomass EMC is lower in pretreated biomass. This demonstrates that both dry and wet torrefied pretreated biomass are more hydrophobic than raw biomass. Aslam et al. (2019) assessed on enhancement of fuel characteristics of rice husk via torrefaction process and the rice husk was torrefied at 200°C, 250°C and 300°C for 10, 30, 90 and 150 minutes under non-oxidative environment. The torrefaction process reduced the swelling tendency of biomass in water from its initial value of 308% to 92%.

III. METHODOLOGY

Sample preparation- For this study, gram stalk (GS) biomass sample were chosen and it is collected from institutional farm of MPUAT, Udaipur. The collected sample were sun dried for 24 hours. After that sample were grounded and passed through the 750µm size sieve. The torrefaction process is better suited to smaller particle sizes due to more effective heat transfer. To avoid moisture absorption, the sample was placed in an airtight plastic bag.

The biomass torrefaction unit in the bioenergy lab was used for the torrefaction experiment. In this case, gram stalks were used as the feedstock, and an industrial oil burner was used to provide the process heat for the biomass's external heating. Torrefaction reactor was initially prepared for three replications at temperatures between 200°C, 250°C, and 280°C. About 10 kg of gram stalk were fed to the reactor for torrefaction. The raw gram stalk was indirectly heated continuously for 10 min duration. The torrefied sample was prepared at various temperatures, sealed in a plastic bag, and kept at room temperature in a desiccator until the analysis was completed. Thereafter, the proximate analysis and calorific value of biomass were carried out at the department of renewable energy engineering, CTAE, Udaipur. The higher heating value (HHV) shows the amount of energy released from biomass when subjected to the combustion process. As the calculation of HHV is very expensive through experimental methods. So, for this study, the HHV of gram stalk was calculated using two different correlations. The first correlation is taken from Nhuchhen and Salam (2012) which has average absolute error of 9.43%. The second correlation is taken from Sheng and Azevedo (2005) with average absolute error of 3.65%.

The correlations which have been used in this study is given below-

$$\text{HHV 1} = 19.2880 - 0.2135\text{VM/FC} - 1.9584\text{ASH/VM} + 0.0234\text{FC/ASH}.$$

$$\text{HHV 2} = -3.0368 + 0.2218\text{VM} + 0.2601\text{FC}.$$

Hydrophobicity Procedure-

In this study, investigation of hydrophobicity of raw and torrefied biomass was done for three different time duration. It is measured according to the international standard ASTM D570. Three readings of each sample were taken for each time duration. And after that average value of the reading was taken. The hydrophobicity of raw and torrefied biomass was determined by immersion testing. About 10g sample of biomass sample was taken for each sample with particle size <1mm and immersed in water for different time duration (2 hr, 24 hr and 48 hr) in deionized water at room temperature in a sintered glass filter. After that the biomass was air dried for 1 hour prior to determining their moisture content. The ration of moisture uptake for samples was calculated using the difference in their weight between before and after treatment.

$$\text{water absorption\%} = \frac{W_1 - W_2}{W_1} \times 100$$

Where,

W₁ = Weight of sample before treatment, gm

W₂ = Weight of sample after treatment,

IV. EXPERIMENTAL RESULTS

Agriculture Residue and Torrefied Product- Figure 1 shows the colour of biomass before and after torrefaction experiments. The torrefied products are more brownish in colour than raw biomass. As the torrefaction temperature increases, the colour of the biomass changes from yellow to dark brownish.



I.



Fig. 1. Raw and torrefied gram stalk at different temperatures (a) Raw gram stalk (b) Torrefied gram stalk at 200°C (c) Torrefied gram stalk at 250°C (d) Torrefied gram stalk at 280°C

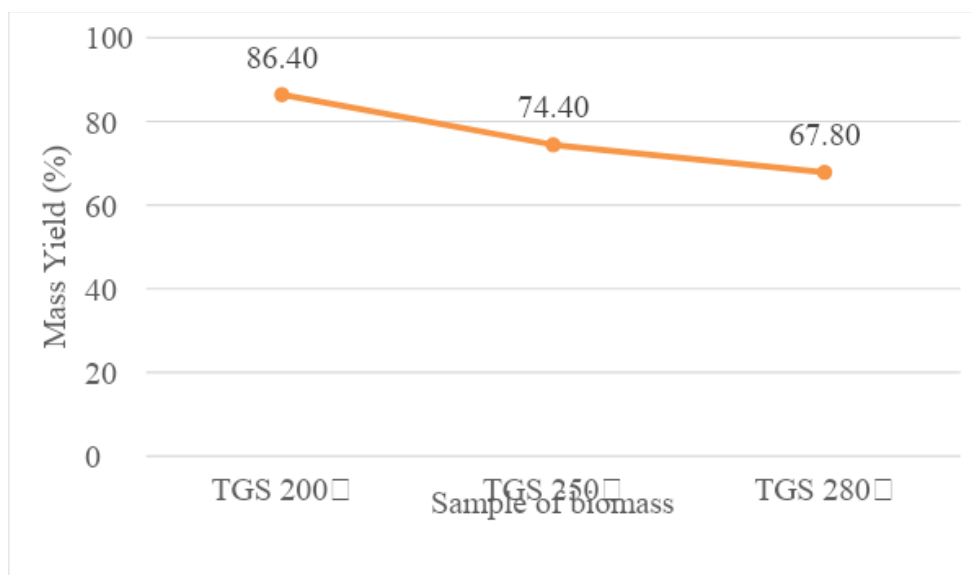
Proximate Analysis and higher heating value- Table 1 shows the influence of torrefaction temperature on proximate analysis of gram stalk. It presents the proximate analysis of all torrefied sample, raw biomass sample and higher heating value also at different experimental condition. It can be seen from table that the moisture content and volatile matter content decreases as the temperature of torrefaction increases. However, the ash content and fixed carbon content increases with the increase in temperature. The raw gram stalk has 19.77% fixed carbon and 70.08% volatile matter and after the torrefaction of raw biomass at different temperature condition, a decrease in volatile matter up to 52.45 % and a rise in fixed carbon up to 38.23% was observed. Devolatilization reaction which takes place during torrefaction may be the reason behind reduction of volatile matter in torrefied gram stalk and the higher fixed carbon content will lead to greater heat production, when the torrefied fuel is burned as reported by Aslam *et al.* (2019).

The HHV value of raw and torrefied gram stalk is calculated using two different equation and the results obtained shows that higher heating value of biomass increases as the temperature of torrefaction increases. It increases from 18.47 MJ/kg (raw gram stalk) to 18.82 MJ/kg (Torrefied gram stalk 280°C), obtained by using first equation. And by using second equation the value of HHV increases from 17.65MJ/kg (raw gram stalk) to 18.54MJ/kg (Torrefied gram stalk 280°C). Due to the increase in relative concentration of the C-C and C-H bonds following the loss of the C-O link during torrefaction, the HHV of torrefied straw increased with the increase in torrefaction temperatures.

Table 1. Proximate analysis and calorific value of raw and torrefied biomass

Sample	Raw gram stalk	Torrefied gram stalk 200°C	Torrefied gram stalk 250°C	Torrefied gram stalk 280°C
MC	4.80	2.84	1.80	1.50
VM	70.08	68.07	62.57	52.45
Ash	5.35	6.28	6.51	7.82
FC	19.77	22.81	29.12	38.23
HHV 1 (MJ/Kg)	18.47	18.56	18.73	18.82
HHV2 (MJ/Kg)	17.65	17.99	18.42	18.54

Mass and Energy yield- Figure 2 and 3 presents the influence of the temperature on mass and energy yields of gram stalk, the percentage of mass and energy yields continually decreases with increases in the torrefaction temperature and torrefaction has more effect on temperature and it could be explained by the decrease with moisture content and volatile matter content of the biomass. Because of the decomposition of some reactive components of the hemicelluloses, there is a significant mass loss at the beginning. when the torrefaction temperature increases, mass yield of the gram stalk decreases from 86.40% to 67.80%. The energy yield decreases from 86.82% to 69.08% and from 88.06% to 71.72%.

**Figure 2. Mass yield of torrefied biomass sample**

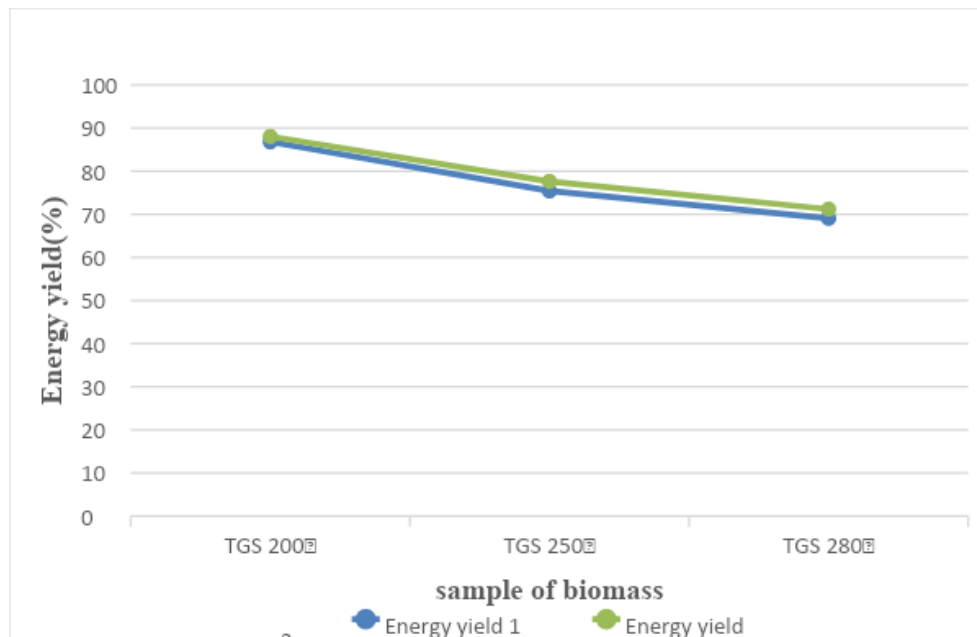


Figure 3. Energy yield of torrefied biomass sample

Hydrophobicity Characteristics - One of the most serious issues with raw biomass is its hydrophobic nature. Even after drying, biomass easily absorbs moisture from the atmosphere. Because of the energy required to evaporate the moisture during combustion or gasification, extended storage of biomass is prohibitively expensive. Torrefaction enhances this property of biomass by decreasing its hydrophobicity. Experiments were conducted to measure the reduction in hydrophobicity by immersing the biomass and torrefied biomass in water for 2hr, 24 hr and 48 hr than its moisture content was measured. It is observed that a specimen torrefied at a higher operating temperature result in a lower moisture absorption. The total moisture absorption is also found to be biomass-specific. Figure 4 shows the ability of moisture absorption in terms of percentage with respect to sample of biomass. It is observed that moisture absorption of pretreated biomass sample decreases as the temperature of torrefaction increases. Samples torrefied at higher temperature absorbs less moisture as compared to raw biomass which is probably due to depolymerization of long chain polysaccharides molecules as per Aslam *et al.*, (2019). In figure 4 it is shown that raw biomass absorbs water lowest at 2 hr and highest at 24 hr, after 48 hr water absorption reduces. Raw biomass readily absorbs moisture due to presence of its hydroxyl group (-OH) groups which forms hydrogen bonds to retain additional water. And after immersing the raw biomass up to 48 hours there is reduction in moisture absorption is observed. The water absorption trend shown by torrefied gram stalk varies with respect to the different process conditions.

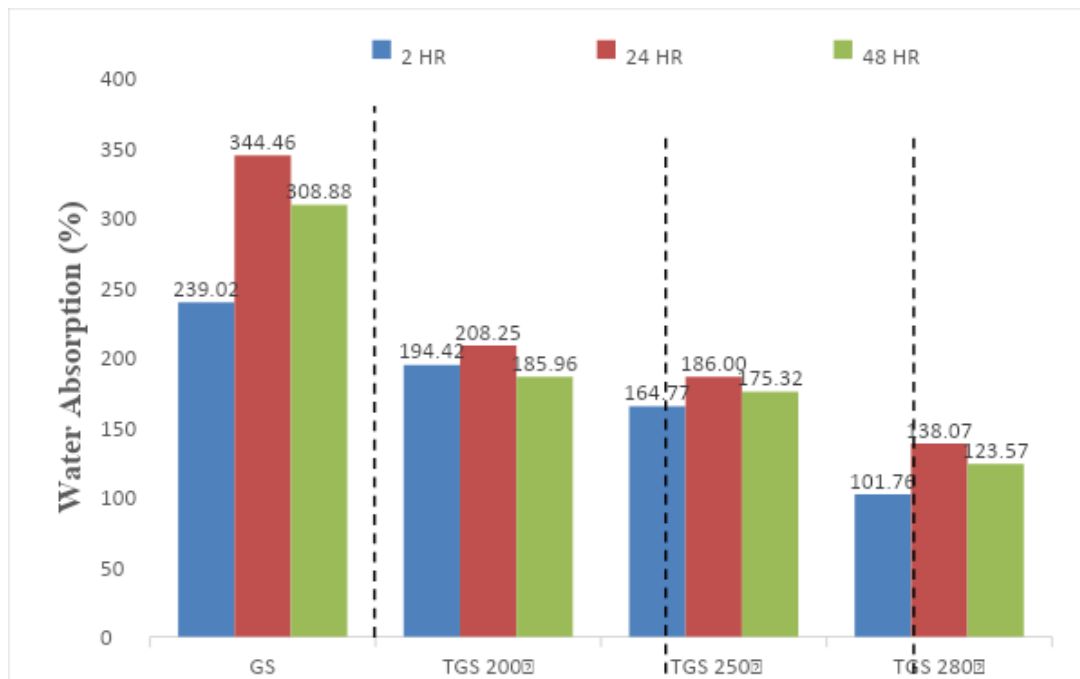


Figure 4. Water absorption (%) of raw and torrefied gram stalk

The torrefaction process destroys the OH groups and due to this its capacity to absorb water decreases. Additionally, due to the chemical rearrangement during torrefaction process, nonpolar unsaturated structures are formed in biomass after torrefaction and it prevents condensation or absorption of water inside the pores as reported by Basu (2018). The absorption capacity of samples torrefied at higher temperature that is at 280°C observed to be more hydrophobic in nature, it absorbs about 101.76%, 138.07% and 123.57% of moisture at 2hr, 24 hrs and 48 hrs respectively. This further demonstrates that torrefaction is a method that can solve the classical problem of moisture absorption by biomass during storage.

V. CONCLUSION

Torrefaction greatly improved the thermophysical properties of gram stalk. Torrefaction of biomass yields a solid fuel with lower moisture and higher energy contents compared to those in a fresh biomass. This directly reduces the transportation cost of the biomass fuel. Investigation on hydrophobicity was done for three different duration 2hr, 24 hr and 48 hr by doing water immersion test. Biomass samples were fully immersed in deionised water for selected duration, after that it is filtered out and air dried for 1 hour before calculation. Raw biomass absorbs more moisture than the torrefied biomass. Moisture uptake in biomass increases up to 24 hours and after 48 hours, moisture absorption reduces, this indicates that after 48 hours, biomass was not absorbing moisture. Mass yield and energy yield is calculated after torrefaction of gram stalk at different temperature (200°C, 250°C and 280°C). Mass yield decrease as the temperature of torrefaction increases from 86.40% to 67.80%. Energy yield also decreases because it is dependent on higher heating value of biomass and mass yield. It decreases from 86.82% to 69.08%. Hydrophobicity of raw and torrefied gram stalk is investigated at three different durations (2hr, 24hr and 48hr). It shows that raw biomass absorbs more water than the torrefied biomass, as raw biomass contains hydroxyl group that



form hydrogen bonds to retain additional water and torrefaction process destroys the OH group and due to this it reduces its capacity to absorb water. The moisture absorption increases up to 24 hr and reduces after 48 hr. After 48 hrs, less moisture content absorbs than 24 hr. This is due to saturation of hydroxyl group present in the biomass or biomass starts losing the absorbed water after some time on its own.

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Impact Factor: 8.118



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