A comparative study on the properties of different paper mill sludge treated by the torrefaction process

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Abstract - This paper represented the physical properties of three different types of paper mill sludge: agro-residue-based, recycle waste-based, and wood-based. On the basis of these physical properties, agro-based paper mill sludge was selected for further treatment by torrefaction in a fixed-bed tubular-type gasifier at different temperatures (225 °C–300 °C) with different residence times (3 min and 5 min). By performing numerous trials and studying the physical and lignocellulose properties of torrefied sludge, it was found that the appropriate temperature and residence time for pre-treatment of sludge were 275 °C and 3 min, where in physical properties, fixed carbon, volatile matter, and HHV were highest and increased by 88.02 %, 11.71 %, and 21.52%, respectively, and ash, which was lowest, and moisture decreased by 5.55% and 68.33%, respectively. In lignocellulose properties, the quantity of lignin was recorded as the highest and increased by 18.79%.

Keywords: Torrefaction, Paper Mill Sludge, Characterization, Physical Properties, Lignocellulose Properties.

I. INTRODUCTION

The pulp and paper industry is one of the major industries; India contributes 3.5% of world paper production and 2% of world trade production. In 2011, paper production was 15.3 million metric tonnes by 825 mills; it was crossed 16.7 million metric tonnes in 2016–17 and is further projected to be 39.7 million metric tonnes in 2026–27[T.R.K.C. Doddapaneni,et al., (2022)]. In India, the paper industry is classified in two ways: by production capacity (Large, medium, and Small scale mills) and by kind of raw material (Agro-residue-based, Wood/forest-based, and Recycle/wastepaper-based mills). According to production capacity, paper production by mills greater than 100,000 TPA is known as large scale, production in the range of 10,000–100,000 TPA is medium scale, and production below 10,000 TPA is classified as small scale. Agro-based mills contribute 11% shares by using bagasse, wheat straw, rice husk, and rice straw as raw materials; wood and forest-based mills contribute 24% shares; and recycle and paper waste mills contribute 65% shares in the total production of paper[T.R.K.C. Doddapaneni,et al., (2022)].In the thermochemical process, raw material is heated in an inert atmosphere and/or a limited oxygen atmosphere at high temperature to generate products: bio-char in solid form[T.R.K.C. Doddapaneni,et al., (2022)].], product gas in gaseous form[J. Makwana et al, (2015)], and bio-liquid in liquid form[J.M. Reckamp,et al., (2014)]. The productivity of the desired product in thermochemical conversion depends on the temperature range, residence time, and reactor operating atmosphere[S. Modak,et al., (2023)]. Thermochemical conversion is classified into three processes: torrefaction, pyrolysis, and gasification, which are further distinguished by temperature range, residence time, and process parameters of the reactor[D. Singh et al., (2020)]. Torrefaction mostly operates in the temperature range of 200 °C–300 °C; it is also defined as the pre-treatment process of raw materials. It removes moisture, changes the physical, chemical, and lignocellulose properties of the raw material, and generates low-weight, high energy density, hydrophobic, and long-term sustainable biochar[D. Singh, A. Raizada,et al., 2022].

Characteristics of paper sludge are distinguished as physical properties, chemical or elemental properties, and lignocellulose properties. The physical properties of sludge define the moisture, ash, volatiles, and fixed carbon of the material. Paper sludge, which is segregated from wastewater by waste water treatment plants, has high moisture contents ranging from 65% to 85% and also a high ash content of 40% to 60% on a dry basis. Volatile matter and fixed carbon are in moderate and low ranges around 45–55% and 1.5–5.5% on a dry basis, respectively[P. Mohanty, et al., 2014]. The large amount of ash in it makes it useless material for further utilisation. Another major problem with sludge is the very small amount of fixed carbon. The main function of the torrefaction process is the generation of carbonised material, which can be either used for thermal and power production by blending with coal, charcoal, and other materials or for soil segregation purposes[D Singh el at., 2021].

The objective of this work is to study the influence of the dry torrefaction process with different temperatures and residence times in a fixed bed reactor on the behaviour of physical properties (Moisture, Ash, Volatile Matter, and Fixed Carbon) and lignocellulose properties (Lignin, cellulose, and Hemicellulose) of paper mill sludge.

Material Selection& Characterization

Raw material that is sludge selected from three different paper mills of the same state, Uttar Pradesh, in India: an agro-residue-based large-scale mill; a wood/forest-based large scale mill; and a recycle/paper waste-based small scale mill. Sludge brought from these paper mills is generated by different raw materials, so it has different properties.

Characterization of paper mill sludge

To study their characteristics: proximate analysis and lignocellulose analysis, different testing procedures were performed after complete open sundry to evaporate extra external water from the sludge.

Proximate analysis is used to examine the inherent physical constituents of materials like moisture, ash, volatile matter, and fixed carbon contents of sludge, was analysed by ASTM D 3173-11, D 3174-02, D 3175-02, and D 5142-02a, methods respectively[D. Singh et al., (2020)].

Lignocellulose properties describe the quantity of polymers (lignin, cellulose, and hemicellulose) in biomass. To calculate these contents in raw materials and torrefied material, used the TAPPI (T 222 om-02),TM I-A11 2001, and TM I-A9 2001 [D. Singh et al., (2020)].

Table 1 shows the difference between these properties in three different sludge types: agro-residue-based sludge, wood-based sludge, and recycled paper mill sludge. Based on the study of these properties, one sludge, i.e., agro-residue-based paper mill sludge, was selected for further torrefaction.

Table 1: Physical properties of the different paper mill's sludge.

Sludge	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed Carbon (%)	HHV (MJ/kg)
Wood based paper mill Sludge$^{(AR,wt)}$	62.39	49.16	19.03	-	-
Recycle paper mill sludge$^{(AR,wt)}$	68.64	57.84	13.02	-	-
Agro-residue based paper mill sludge$^{(AR,wt)}$	88.24	44.17	5.76	-	-
Wood based paper mill Sludge$^{(SD,db)}$	1.00	50.71	47.50	0.78	7.29
Recycle paper mill sludge$^{(SD,db)}$	1.60	57.93	40.43	0.04	5.86
Agro-residue based paper mill sludge$^{(SD,db)}$	6.87	46.75	43.94	2.44	7.35
AR: As received Sludge, **SD**: Sun Dried sludge, **wt**: Wet basis, and **db**: Dry basis					

Experimental Setup and procedure

A fixed-bed tubular-type reactor was used for torrefaction of agro-residue-based paper mill sludge. Nitrogen was supplied through the top of the reactor and came out of the bottom of the reactor. A condenser and a conical flask were attached at the bottom of the reactor to condense and collect moisture, condensable volatile matter, and non-condensable gases during the torrefaction process, which was carried out by carrier gas (N_2). A conical feeding hopper was connected at the top of the reactor for smooth and proper feeding of sludge.Experiments were carried out at different temperatures, from 225 °C to 300 °C, with a difference of 25 °C and different residence times of 3 and 5 minutes, respectively. Agro-based sludge was fed through the hopper into the reactor and stayed in the reactor for different resident times (3 min and 5 min) at different reactor temperatures. After completion of residence time, heaters were switched off and nitrogen supply stopped.

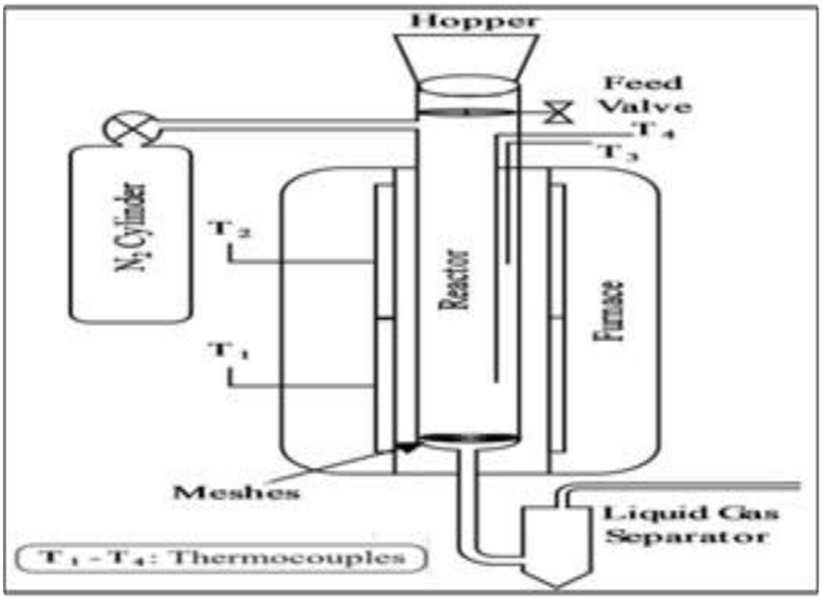

Figure 1: The fixed-bed tubular-type reactor.

II. RESULT AND DISCUSSION

Physical properties of three different paper mill sludge

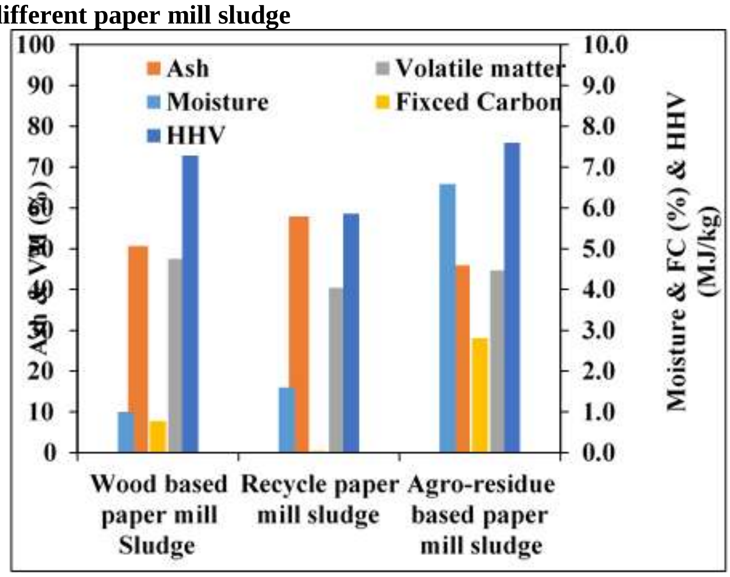

Figure 2: Physical properties of Sundried different paper mills raw sludge.

Figure 2 shows the physical properties (moisture, ash, volatile matter, fixed carbon in percentage, and HHV in MJ/kg) of three different paper mill sludges after an approximate one-week open sun dry. Figure 2shows that after sun drying, when the moisture of all sludge almost reaches equilibrium with atmospheric humidity, the moisture percentage in agro-residue-based paper sludge is larger than in others. Though, it had high moisture, it also contained a high percentage of fixed carbon in comparison to the other two paper mill sludges. Fixed carbon in recycled paper mill sludge was the smallest, around 0.04 % (Table 1). Heating value: the amount of energy in sludge, which has been described in High Heating Value (HHV) in MJ/kg, was highest in agro-residue-based paper mill sludge, followed by wood-based paper mill sludge, and smallest in recycle-based paper mill sludge. Recycled paper mills had the highest ash percentage, followed by wood-based paper mill sludge, and agro-residue-based paper mill sludge had the smallest ash percentage. High ash content in sludge is undesirable for the conversion process of biomass to biofuel[D. Singh, A.

Raizada,et al., 2022]]. On the basis of these physical properties, the examination found that agro-residue-based paper mill sludge was more suitable for further use in thermo-conversion appliances.

Change in physical properties for3 min residence time

Figure 3: Torrefaction temperatures effect on physical properties of ABS.

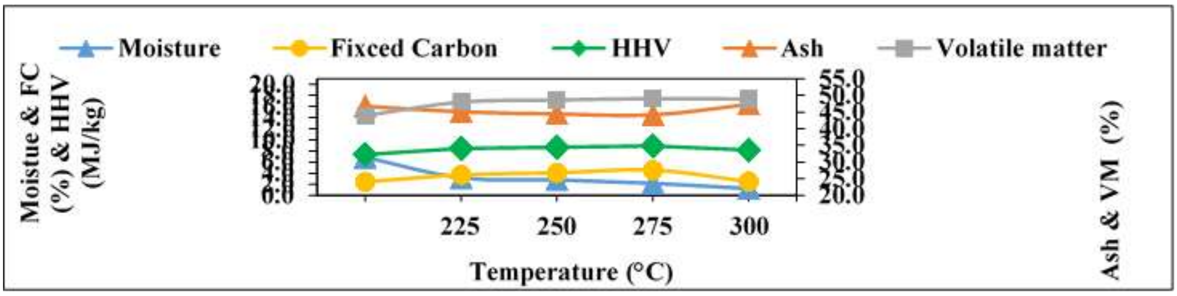

Figure 3, depicts the influence of the torrefaction process at different temperatures (225 °C–300 °C) with a 3-minute residence time on the physical properties of agro-residue-based sludge (ABS). From the figure3, it can be clearly seen that at 225 °C, sludge went through a dry process because at this temperature most of the moisture was reduced. Due to the reduction of moisture, other properties such as volatile matter, ash, fixed carbon, and HHV of sludge were improved. That means at 225 °C, the reactor behaved like a dryer. Further change in temperature from 225 °C to 250 °C did not show such a change in moisture, but ash, fixed carbon, and HHV of sludge improved, which indicated that sludge came under the torrefaction process and exothermal reactions played their role in breaking down molecular bonding of material[P. Mohanty,et al,2022]. At 275 °C, found the highest amount of fixed carbon, HHV and volatile matter in torrefied sludge with the lowest value of ash. A further change in temperature from 275 °C to 300 °C performed an extreme exothermal reaction, due to which a large change in properties was noticed. The highest ash content was found in torrefied sludge at 300 °C, which was not favourable for torrefied sludge's.

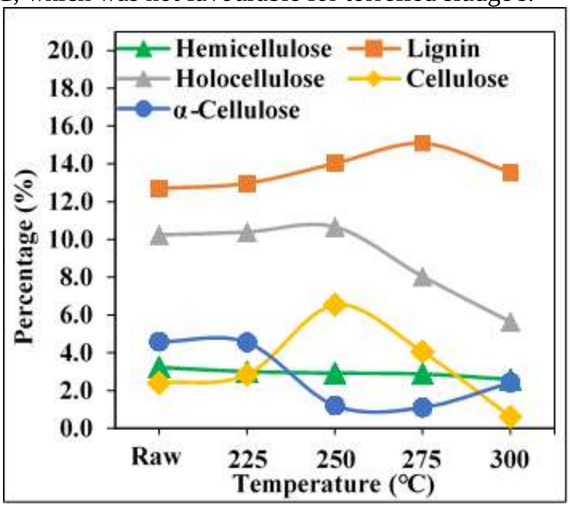

Figure 4: Torrefaction temperatures effect on lignocellulose properties of ABS.

Change in lignocellulose properties for 3 min residence time

From the physical properties of torrefied sludge mentioned above, at 225 °C, the reactor behaved like the drier, so no such change was noticed at this temperature in the lignocellulose properties of torrefied sludge, as shown in Figure 4. Hemicellulose has the lowest molecular weight of hydrocarbons in comparison to cellulose and lignin. So at low temperatures, it can easily break down and degrade[D. Singh, A. Raizada,et al., 2022]]. The same happens in this case; at the lowest temperature (225 °C), only hemicellulose decreased, as shown in figure 4. A large and favourable change in lignocellulose properties was seen at temperatures of 250 °C and 275 °C. At 250 °C, a pre-torrefaction process occurred that broke down the lignocellulose structure of the material, degraded it, and removed it. At this temperature, a severe change was found in the contents of cellulose and alpha-cellulose. Lignin, which has the highest molecular weight bonds, does not affect such a temperature range, so the reduction of hemicellulose and alpha cellulose in torrefied material causes an increase in the amount of lignin in torrefied material[D. Singh, A. Raizada,et al., 2022]]. At 275 °C, cellulose, hemicellulose, and alpha cellulose were degraded, andthe highest hike was noticed in lignin content in torrefied sludge at 275 °C. Further change in temperature from 275 °C to 300 °C, where extreme exothermal reactions occur, which degrade the lignin contents of the sludge[4, 9, 15, 16, 19].

Change in physical properties for 5 min residence time

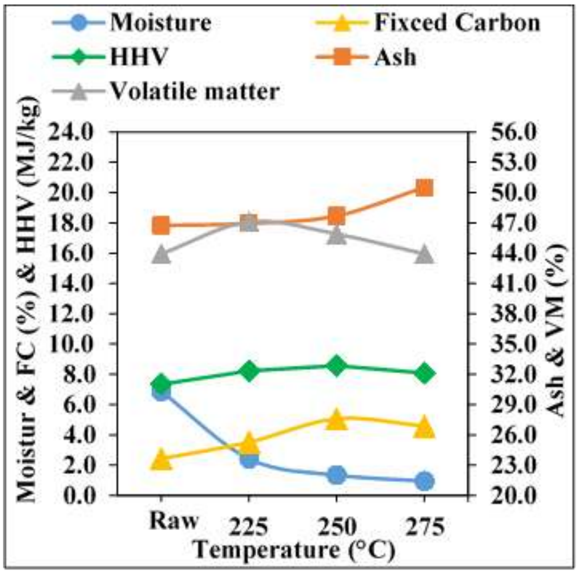

Figure 5: Torrefaction temperatures effect on physical properties of ABS.

Figure 5, shows theeffects of 5-minute residence time at the 225°C–300°C temperature range on the physical properties of agro-residue-based sludge (ABS). Increased in residence time increased the heat contact time of the material[S. Yadav, P. et al., 2022], which started the torrefaction process at 225 °C with a 5 min residence time. Volatile materials were found in the highest amounts at this temperature. Further change in temperature from 225 °C to 250 °C, though increasing fixed carbon and HHV of torrefied sludge, also showed a hike in ash content, which was not favourable for the utilisation of bio-char as energy in thermos-conversion applications. Furthermore, the increase in temperature from 250 °C to 275 °C showed mitigation in fixed carbon, volatile matter, and HHV of the torrefied sludge. This mitigation was found due to the highest ash content in torrefied sludge. At 275 °C with a 5-minute residence time, sludge particles could not hold and resist going through severe exothermal reactions, which drastically changed the properties of the material.

Change in lignocellulose properties for 5 min residence time

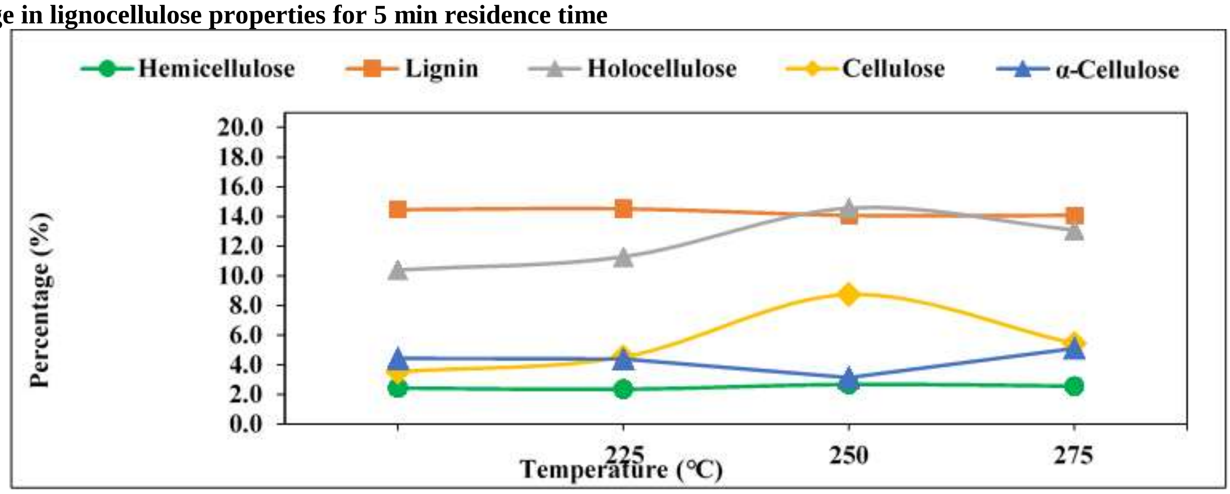

Figure 6: Torrefaction temperatures effect on lignocellulose properties of ABS.

Figure 6 shows the effect of a 5-minute residence time on the lignocellulose properties of sludge. From the figure 5 & 6, it can easily be determined that at the lowest temperature, i.e., 225 °C with a 5 min residence time, there was not a great influence noted other than moisture, which increased the quantity of lignin, but increase in residence time of 3–5 min, along with hemicellulose degradation, some parts of alpha and lignin were also degraded. Alpha cellulose and lignin may convert to lighter hydrocarbons and increased cellulose contents[J. Makwana,el al., 2015]. A further increase in temperature, i.e., 275 °C, performed severe exothermal reactions that degraded lignin and alpha contents badly and converted them into lighter polysaccharides, which caused an increase in the contents of hemicellulose and cellulose. At 300 °C, degradation and conversion of heavier to lighter hydrocarbons of lignin fibres continued, which increased the quantity of alpha cellulose, but at this temperature, large degradation was found in cellulose fibres, as shown in figure 6.

III. CONCLUSION

By examination of the physical properties of different raw materials: agro-residue-based, recycle waste-based, and wood-based paper mill sludge, found that the undesired product, ash, in agro-residue-based paper mill sludge had the lowest quantity, and the favourable product, fixed carbon, was the highest in comparison to other sludge. Hence, the agro-residue-based sludge was selected for further pre-treatment by torrefaction to improve its physical and lignocellulose properties. From the various experimental trails, it was found that the appropriate temperature and residence time was 275 °C and 3 min, respectively, where the highest quantity of fixed carbon, HHV, and volatile matters, which were increased by 88.02%, 11.71 %, and 21.52 %, respectively, and ash and moister decreased by 5.55% and 68.33%, respectively. Lignocellulose properties, the highest quantity of lignin, found increased by 18.79% from raw sludge.

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