

Hydrothermal Carbonization of Different Recycling Paper Mill Waste Streams

Englatina I.N.C. Assis*, Evans M. N. Chirwa, Shepherd M. Tichapondwa

Water Utilisation and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa.
 englatina.assis@gmail.com

Hydrothermal carbonization (HTC) is an attractive technology to address problems associated with moisture-rich pulp and paper sludge generated at South African mills and wastewater treatment plants. In this study, sludge generated from the repulping process, recycling paper process, and primary clarifier wastewater treatment were selected to investigate the potential of HTC to upgrade the feedstock into solid fuel. Experiments were performed in a batch reactor autoclave at different operating temperatures (200 °C, 220 °C and 240 °C), residence time of 3 h, and wet biomass to deionized water ratio of 1:9. Data on the physicochemical characteristics and calorific values of the solid yield, as well as carbon mass distribution, were reported. Results revealed that higher temperatures resulted in hydrochar with higher calorific values from 15.26 to 22.57 MJ/kg, 15.33 to 20.32 for repulping paper sludge and recycling paper sludge, respectively, but lower calorific values (from 9.79 MJ/kg to 7.02 MJ/kg) for sludge from primary clarifier process. The proportions of fixed carbon for hydrochars obtained at 245 °C were 5-7 times greater than the raw samples, but solid mass yield decreased with an increase in reaction temperatures for all feedstocks. Analysis of the carbon mass balance revealed that, for all HTC treatments, the majority of the carbon fraction was retained in the hydrochar. HTC was proven to be an efficient technology for upgrading sludge generated at pulp and paper mills in South Africa into hydrochar with enhanced properties with a variety of applications including solid fuel, energy storage, soil amendment, adsorbent and catalyst.

1. Introduction

Significant wastes consisting of high inherent moisture and lignocellulosic components are constantly generated at pulp and paper industries in South Africa in the form of sludge. These wastes are typically composed of particulate wastes, organic and inorganic substances (Kaur et al., 2020), and are mostly disposed of through incineration, landfilling, and land-farming applications (Majewski and Jääskeläinen, 2004). These practices are known to cause major health problems and environmental degradation due to the emission of greenhouse gases (GHG) into the atmosphere, and the leaching of toxic substances such as heavy metals into the ground and water systems. Thus, there is a concern to decrease the hazardous nature of pulp and paper mill wastes by adopting clean technologies to divert the wastes from landfills for beneficial applications.

Energy can be recovered from pulp and paper mill sludge through thermochemical, biochemical and mechanical processes. Hydrothermal carbonization (HTC) is an emerging technology that upgrades unconventional substrates into carbon-rich products without the need for pre-drying (Funke and Ziegler, 2010). The exothermic process occurs in the presence of liquid water, at temperatures ranging from 180-260 °C, and self-generating pressure which typically ranges from 1 to 3 MPa (Merzari et al., 2018). The resulting coal-like material, commonly referred to as hydrochar, has good dewatering property, improved hydrophobicity, and, when dried, has higher calorific value compared to the initial feedstock (He et al., 2013). The hydrochar obtained from the HTC treatment has a variety of benefits and applications in solid fuel, soil amelioration, low-cost adsorbent, catalyst, and contaminant removal (Fang et al., 2018).

Several authors have reported the application of HTC on a variety of organic substrates including raw sludge from municipal wastewater treatment plant (Chen et al., 2020), raw olive mill waste (Volpe et al., 2018), and wood biomass (Stirling et al., 2018). However, the HTC process on different pulp and paper mill sludge has not

been extensively studied and reported. In this work, the effect of subcritical water temperature on HTC of sludge generated from the repulping process, recycling paper process, and primary clarifier wastewater treatment was investigated to assess the potential of HTC to upgrade the pulp and paper sludge generated at South African mills, into a more uniform hydrochar with enhanced fuel properties. The physicochemical characteristics of the hydrochar were reported.

2. Materials and methods

This section describes the hydrothermal carbonization procedure and solid product analysis. The reactions were conducted in a closed system and autogenous pressure. The pressure inside the reactor was not monitored for the experiments and was maintained autogenic with the vapor pressure of water at the corresponding reaction temperature. To ensure reproducibility and consistency, the experiments were conducted in triplicate and the analysis was conducted in duplicate.

2.1 Hydrothermal Carbonization

HTC experiments were conducted on three different substrates, namely, raw rejects from the repulping process (RF), final waste sludge from the recycling paper process (RPS), and paper sludge generated at the primary clarifier wastewater treatment (PCS) with moisture contents of 21.1 %, 23.4 % and 14.3 %. For each experiment, 10 g wet sample was mixed with 90 mL of deionized water, stirred manually for 3 min, and transferred to a 130 mL Teflon-lined alloy steel reactor autoclave designed at the University of Pretoria (South Africa). Once sealed and bolted, the reactor was placed into a conventional oven where it was heated to the desired temperature of 205 °C, 225 °C and 245 °C, followed by an isothermal hold of 3 h. Once the carbonization time elapsed, the reactor was removed from the oven, placed in a cold room at 4 °C, and allowed to cool down to room temperature in 2 h. The produced hydrochar was filtered through a cellulose phosphate-free filter paper with 4-12 µm average retention capacity (grade MN 615, USA) and dried in an oven at 80 °C for 24 h. The hydrochar yield was calculated according to Eq(1):

$$\text{Hydrochar yield (\%)} = \frac{\text{mass of dried hydrochar}}{\text{mass of dried feedstock}} \times 100 \quad (1)$$

The dried samples were ground with a mortar and pestle, sieved to a particle size less than 250 µm, and stored in a desiccator for further characterization.

2.2 Feedstock and Hydrochar Characterization

The elemental CHNS composition of the samples was assessed using a Flash 2000 Elemental analyzer (Thermo Fisher Scientific) at the University of Johannesburg (South Africa). The oxygen weight percentage was estimated according to Eq(2):

$$\text{O (\%)} = 100 - (\text{C} + \text{H} + \text{N} + \text{S}) \quad (2)$$

A thermogravimetric analyzer (Hitachi STA300 TGA-DTA) was used to determine the residual moisture (RM), volatile matter (VM), fixed carbon (FC), and ash content of the samples according to ASTM D7582-15. The calorific values based on the higher heating values (HHV) were determined using a bomb calorimeter (Parr 6200 Oxygen Bomb Calorimeter) according to ASTM D5865-19. The higher heating values were converted to dry basis according to Eq(3):

$$\text{HHV}_{\text{d.b.}} (\text{MJ/kg}) = \frac{\text{HHV}_{\text{meas}}}{1 - X_{\text{RM}}} \quad (3)$$

Where HHV_{meas} and X_{RM} represent the measured HHV from the bomb calorimeter and weight fraction of the residual moisture present in the hydrochar.

3. Results and discussion

In this section, the data obtained using the methodology aforementioned are presented. The effect of reaction temperature on the visual aspects, elemental and proximate composition, the energy content of the hydrochar, as well as the carbon mass weight distribution between solid, liquid and gas products, are discussed.

3.1 Visual Assessment

The physical appearance of dried feedstock and dried hydrochars obtained at different carbonization temperatures are illustrated in Figure 1. It is evident that HTC resulted in hydrochar with physical characteristics distinctive from the initial samples. Compared to the raw samples, hydrochars could easily be ground into smaller particles by mortar and pestle. In addition, the increase in carbonization temperatures resulted in hydrochar with more hydrophobic properties. This was observed through the increased rate of filtration and decreased water-holding capacity at higher temperatures, as the amount of process water collected during filtration which was minimum at 205 °C. When the temperature was ≥ 225 °C for RF and RPS, the produced hydrochars were darker in color with more uniform and compacted particles, however, these characteristics were not significantly distinctive for PCS at ≥ 225 °C. In general, the change in characteristics is due to reaction mechanisms occurring during HTC conversion, which are further discussed in the subsequent subsections.

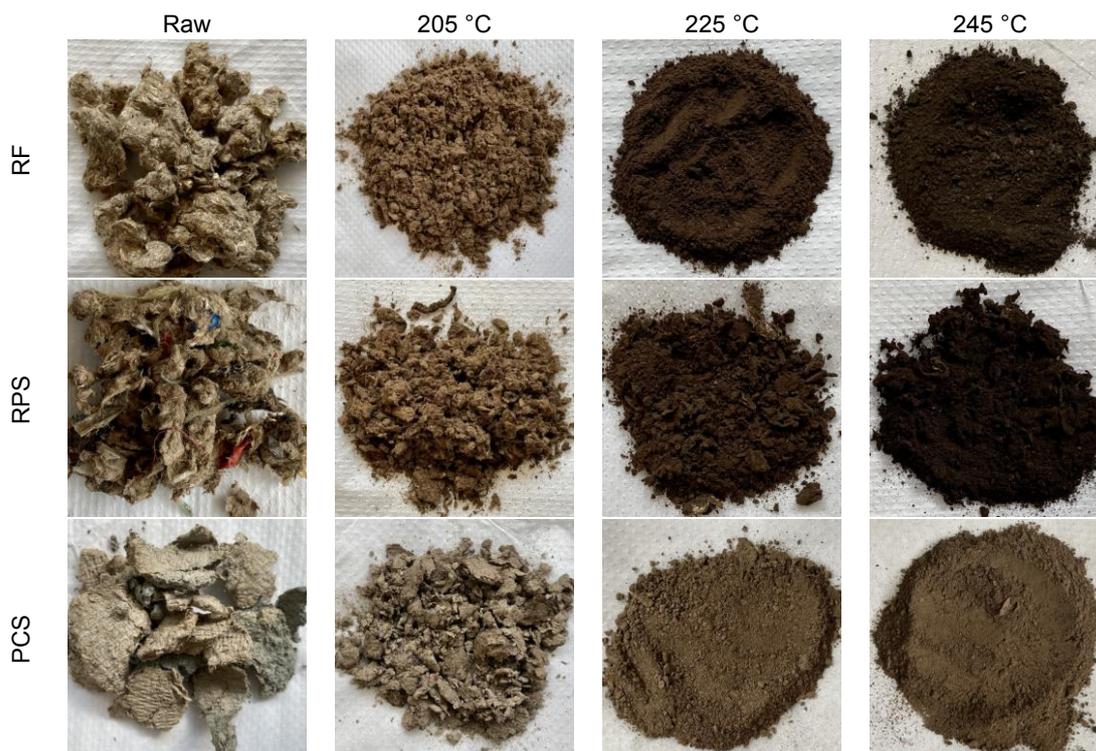


Figure 1: Samples of dried substrates and dried ground hydrochars obtained at 205 °C, 225 °C and 245 °C.

3.2 Ultimate and proximate analysis

HTC treatment resulted in hydrochars with different physicochemical properties compared to the untreated samples. The ultimate and the proximate analysis are presented in Table 1. In comparison to the raw samples, the carbon content of the hydrochars increased with an increase in reaction temperature (except for PCS), whilst the oxygen content simultaneously decreased for all samples. This change is mainly attributed to dehydration and decarboxylation reactions which hydroxyl and carboxyl groups are removed from the solid phase and released in the form of H_2O and CO_2 (Wang et al., 2018) as a result, a more aromatic carbon is formed in the hydrochar (He et al., 2013). The increase in carbon and decrease in oxygen content contribute to the increase in higher heating value (HHV). When comparing the hydrochars obtained from the three different substrates, HTC of RPS produced hydrochars with the highest carbon proportion (60.23 %) at 245 °C, whilst HTC of PCS produced hydrochars with the lowest carbon content. Regarding the sulfur content, at 205 °C $< T \leq 225$ °C, the sulfur content reduced to the lowest values corresponding to < 0.001 %, 0.44 % and 0.001 % for RF, RPS and PCS. This is due to the formation of sulfur oxides during HTC which are then dissolved in the process water (Lin et al., 2015). At 245 °C the sulfur content slightly increased to 0.41 %, 0.53 % and 0.41 % for RF, RPS and PCS. This is attributed to the formation of sulfur species precipitate on the surface of the hydrochar (Wang et al., 2020). For solid fuel application of hydrochar, low to no sulfur content is desired as it mitigates the emission of acid rain persecutors such as SO_2 and SO_3 .

The proximate analysis was in agreement with the elemental analysis. The residual moisture (RM) decreased with an increase in reaction temperature, reaching the lowest values of 0.72 % at 245 °C for PCS. This trend confirms the improvement in hydrophobicity properties of the hydrochars. As a result of the increase in carbonization temperature, the volatile matter (VM) content decreased significantly with a simultaneous increase in fixed carbon (FC). These changes are due to the degradation of the lignocellulosic component, mainly hemicellulose and cellulose which start dissolving at 180-220 °C (Wang et al., 2018). This is more predominant at 245 °C where the maximum loss of 66.04 %, 77.67 % and 76.61 % of the initial volatile content for RF, RPS and PCS, respectively, is observed. In contrast, the fixed carbon showed a significant increase. The proportions of fixed carbon for hydrochars obtained at 245 °C were 5-7 times greater than the raw samples. These analyses are in agreement with reported works (Saha et al., 2019a).

The ash content was predominantly inert during HTC treatment. Although it slightly decreased for RF at 205 °C, it generally increased as the reaction progressed, reaching 50.20 % at 245 °C for PCS. This is because, during the degradation of organic substances, the inorganic content is retained in the hydrochars (McGaughy and Reza, 2018). The trend in ash content reported in this study is in agreement with previous work (Saha et al., 2019b). Ash content contributes negatively to the energetic properties of the hydrochar and increases the risk of fouling, scaling, slagging and corrosion in combustion chambers.

Table 1: Ultimate and proximate analysis of raw samples and hydrochars produced, expressed in weight percentage (wt. %) on dry basis (d.b.)

Sample	C (wt. % d.b.)	H (wt. % d.b.)	N (wt. % d.b.)	O (wt. % d.b.)	S (wt. % d.b.)	RM (wt. %)	VM (wt. % d.b.)	FC (wt. % d.b.)	Ash (wt. % d.b.)
RF Raw	39.29	5.12	< 0.001	39.47	2.27	5.21	76.01	10.13	13.87
RF 205 °C	41.26	5.20	0.12	44.75	< 0.001	2.82	63.08	26.96	9.96
RF 225 °C	48.21	5.58	0.15	36.57	< 0.001	2.18	51.56	37.65	10.80
RF 245 °C	51.37	4.76	0.23	28.41	0.42	1.58	25.81	59.98	14.21
RPS Raw	39.28	5.30	< 0.001	40.79	2.37	6.01	77.15	10.59	12.26
RPS 205 °C	42.22	5.22	0.28	40.05	0.45	2.58	55.44	28.33	16.23
RPS 225 °C	47.09	5.50	0.34	26.86	0.44	1.83	42.17	36.62	21.21
RPS 245 °C	60.23	5.57	0.58	5.01	0.53	1.35	21.79	50.12	28.09
PCS Raw	28.04	3.57	< 0.001	34.55	2.34	3.85	63.31	5.18	31.51
PCS 205 °C	26.32	3.00	0.15	29.32	< 0.001	1.41	26.74	32.09	41.17
PCS 225 °C	26.87	3.01	0.14	26.69	< 0.001	1.18	23.73	32.97	43.30
PCS 245 °C	24.24	2.25	0.19	22.70	0.41	0.72	14.81	34.99	50.20

3.3 Calorific values and hydrochar yield

The higher heating value (HHV) is an important characteristic of the hydrochars, and the trend is illustrated in Figure 2, along with the solid yield. As a result of the hydrothermal degradation of organic components of the samples, the hydrochar yield decreased whilst the HHV increased with an increase in reaction temperature. In general, the pulp and paper sludges are mainly composed of lignin, cellulose, and hemicellulose (Kaur et al., 2020). The HHV of lignin is considerably higher than that of cellulose and hemicellulose (Kambo and Dutta, 2015); therefore, the removal of hemicellulose of biomass resulted in hydrochar with increased lignin composition which led to increased energy densification, thus higher HHV. The highest HHV recorded was 22.57 MJ/kg for RF at 245 °C. Unlike RF and RPS, the HHV of PCS decreased with an increase in reaction temperature. A similar trend was also observed by Cantero-Tubilla et al. (2018). The decrease in HHV for PCS is associated with the significant increase of ash retained in the hydrochar, as ash has lower HHV compared to hemicellulose, cellulose and lignin (Kambo and Dutta, 2015), this factor contributed to poor hydrochar properties.

3.4 Carbon mass distribution

The carbon mass balance is presented in Figure 3. The carbon content in the solid phase for RF, RPS and PCS ranged from 53.78-91.26 %, 81.94-83.54 % and 52.44-81.98 %, respectively. The carbon retained in the hydrochar for RF and PCS decreased as the temperature was increased, however, no significant change was observed for RPS. The carbon retained in RPS hydrochar increased from 81.98 % to 88.98 % at 225 °C. The overall results showed that most of the carbon fraction is retained in the hydrochar after HTC treatment.

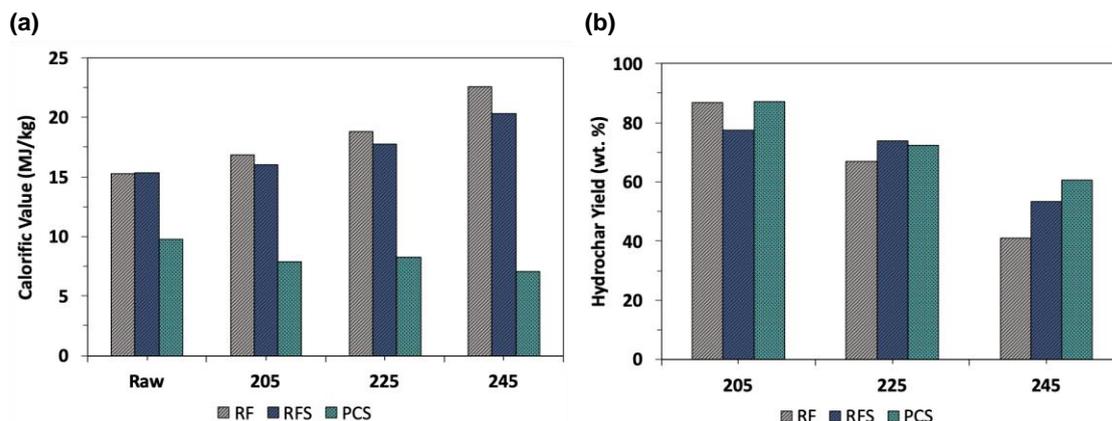


Figure 2: (a) HHV of substrates and hydrochars. (b) Hydrochar yield at different carbonization temperatures

A negligible fraction of carbon was transferred into the liquid phase. It is important to mention that the total organic carbon (TOC) analysis of the liquid products was not conducted immediately after HTC treatment. Although the liquid samples were stored in centrifuge tubes at 4 °C environment, after 24 h, it was observed the formation of black precipitates in the walls of the container and on the surface of the process wastewater. The formation of precipitate could be due to the presence of reactive elements in the liquid phase which were released during HTC treatment. The solids were filtered through 0.25-0.45 μm nylon syringe filters before analysis. The precipitate formation and removal could have contributed to the negligible carbon percentage in the liquid phase after analysis. The carbon fraction in the gas phase was estimated by the difference using the carbon fraction in solid and liquid fractions. From Figure 3, higher reaction temperatures resulted in higher carbon fractions transferred to the gas phase. The highest carbon fractions in the gas phase observed were at 245 °C, corresponding to 45.32 %, 17.10 % and 47.17 % for RF, RFS and PCS.

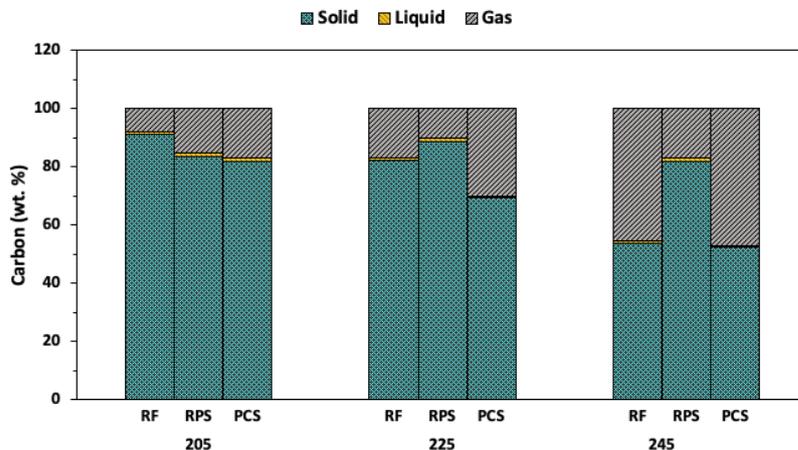


Figure 3: Carbon mass distribution between solid, liquid and gas phases.

Based on the results obtained in this work, PCS was concluded to be an unsuitable substrate for HTC treatment to produce hydrochar for solid fuel applications, due to the physicochemical characteristics observed in the hydrochar produced. This includes decreased carbon content, significantly increased ash content, and lower HHV. However, RF was found to be more suitable for HTC treatment compared to RFS, mainly because the hydrochar produced presented relatively low ash content which is of great importance for solid fuel application. It also presented a relatively high fixed carbon and calorific value increase.

4. Conclusions

In this work, the HTC treatment on three different substrates was investigated at different reaction temperatures. HTC resulted in hydrochars with improved hydrophobicity and physicochemical properties in general. Higher

reaction temperatures led to increased carbon content and decreased oxygen fraction. The highest carbon increase recorded was from 39.28 to 60.23 % at 245 °C for RFS. Similarly, the proximate analysis results showed that higher reaction temperatures decreased the volatile matter content while simultaneously increased the fixed carbon content, thus it contributed positively to the higher heating values whilst the hydrochar yield decreased. The highest HHV recorded was 22.57 MJ/kg for RF hydrochar obtained at 245 °C. The carbon balance revealed that most of the carbon fraction is retained in the hydrochar after the HTC treatment. Among the three substrates, RF was more suitable for HTC treatment as the hydrochars produced contained relatively low ash and higher calorific values. In conclusion, this study demonstrated that HTC can effectively recover hydrochar with enhanced thermal properties to be used as a source of energy, soil amendment, adsorbent or catalyst. In future work, RF will be used to develop a model to predict the hydrochar yield and HHV to determine the optimum process condition (temperature, residence time, and substrate to water ratio) to produce hydrochar with improved solid fuel properties.

Acknowledgments

The author acknowledges Mpact Springs and Neopak for sample provision, and Ministério dos Petróleos Angola (MINPET) for financial support. Funding for experimental work was provided through the Sedibeng Water Chair in Water Utilisation Engineering awarded to Prof Evans M.N. Chirwa of the Water Utilisation and Environmental Engineering Division at the University of Pretoria.

References

- Cantero-Tubilla, B., Cantero, D. A., Martinez, C. M., Tester, J. W., Walker, L. P., Posmanik, R. 2018. Characterization of the solid products from hydrothermal liquefaction of waste feedstocks from food and agricultural industries. *The Journal of Supercritical Fluids*, 133, 665-673.
- Chen, C., Liu, G., An, Q., Lin, L., Shang, Y., Wan, C. 2020. From wasted sludge to valuable biochar by low temperature hydrothermal carbonization treatment: Insight into the surface characteristics. *Journal of Cleaner Production*, 263, 121600.
- Fang, J., Zhan, L., Ok, Y. S., & Gao, B. 2018. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. *Journal of Industrial and Engineering Chemistry*, 57, 15-21.
- Funke, A., Ziegler, F. 2010. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels, Bioproducts and Biorefining*, 4, 160-177.
- He, C., Giannis, A., Wang, J.-Y. 2013. Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior. *Applied Energy*, 111, 257-266.
- Kambo, H. S., Dutta, A. 2015. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renewable and Sustainable Energy Reviews*, 45, 359-378.
- Kaur, R., Tyagi, R. D., Zhang, X. 2020. Review on pulp and paper activated sludge pretreatment, inhibitory effects and detoxification strategies for biovalorization. *Environmental Research*, 182, 109094.
- Lin, Y., Ma, X., Peng, X., Hu, S., Yu, Z., Fang, S. 2015. Effect of hydrothermal carbonization temperature on combustion behavior of hydrochar fuel from paper sludge. *Applied Thermal Engineering*, 91, 574-582.
- Majewski, W., A., Jääskeläinen, H. 2004. Environmental Effects of Emissions. *DieselNet Technology Guide*.
- McGaughy, K., Reza, M. T. 2018. Recovery of Macro and Micro-Nutrients by Hydrothermal Carbonization of Septage. *Journal of Agricultural and Food Chemistry*, 66, 1854-1862.
- Merzari, F., Lucian, M., Volpe, M., Andreottola, G., Fiori, L. 2018. Hydrothermal Carbonization of Biomass: Design of a Bench-Scale Reactor for Evaluating the Heat of Reaction. *Chemical Engineering Transactions*, 65, 43-48.
- Saha, N., Saba, A., Reza, M. T. 2019a. Effect of hydrothermal carbonization temperature on pH, dissociation constants, and acidic functional groups on hydrochar from cellulose and wood. *Journal of Analytical and Applied Pyrolysis*, 137, 138-145.
- Saha, N., Saba, A., Saha, P., McGaughy, K., Franqui-Villanueva, D., Orts, W., Hart-Cooper, W., Reza, M. 2019b. Hydrothermal Carbonization of Various Paper Mill Sludges: An Observation of Solid Fuel Properties. *Energies*, 12, 858.
- Stirling, R. J., Snape, C. E., Meredith, W. 2018. The impact of hydrothermal carbonisation on the char reactivity of biomass. *Fuel Processing Technology*, 177, 152-158.
- Volpe, M., Wüst, D., Merzari, F., Lucian, M., Andreottola, G., Kruse, A., Fiori, L. 2018. One stage olive mill waste streams valorisation via hydrothermal carbonisation. *Waste Management*, 80, 224-234.
- Wang, T., Zhai, Y., Zhu, Y., Li, C., Zeng, G. 2018. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. *Renewable and Sustainable Energy Reviews*, 90, 223-247.
- Wang, Z., Zhai, Y., Wang, T., Peng, C., Li, S., Wang, B., Liu, X., Li, C. 2020. Effect of temperature on the sulfur fate during hydrothermal carbonization of sewage sludge. *Environmental Pollution*, 260, 114067.