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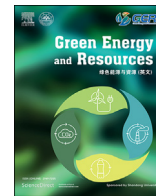
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Research Article

Hydrothermal carbonization coupled with pyrolysis: An innovative approach to digestate management



Ziyi Shi^{a,1}, Sirui Liu^{d,1}, Shule Wang^{a,b,c,*}, Lukasz Niedzwiecki^{e,h}, Marcin Baranowski^e, Michał Czerep^e, Chuchu Tang^f, Sibudjing Kawi^g, Chi-Hwa Wang^g, Jianchun Jiang^{b,c}, Mikael S. Hedenqvist^d, Halina Pawlak-Kruczek^e, Wangzhong Mu^a, Yuming Wen^{a,g,**}, Pär Göran Jönsson^a, Weihong Yang^a

^a Department of Materials Science and Engineering, KTH Royal Institute of Technology, Brinellvägen 23, 114 28 Stockholm, Sweden

^b International Innovation Center for Forest Chemicals and Materials, College of Chemical Engineering, Nanjing Forestry University, Longpan Road 159, Nanjing, 210037, China

^c Jiangsu Province Key Laboratory of Biomass Energy and Materials, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry (CAF), No. 16, Suojin Five Village, Nanjing, 210042, China

^d Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 58, 11428 Stockholm, Sweden

^e Wrocław University of Science and Technology, Wybrzeże Stanisława Wyspiańskiego 27, 50-370 Wrocław, Poland

^f School of Design and Art, Human Institute of Technology, 421001 Hengyang, China

^g Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585, Singapore

^h Energy Research Centre, Centre for Energy and Environmental Technologies, VŠB—Technical University of Ostrava, 17. Listopadu 2172/15, 708 00 Ostrava, Czech Republic

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ABSTRACT

Anaerobic digestion presents a viable approach for managing biodegradable waste. However, the process generates a significant amount of digestate, which, if not appropriately managed, can contribute to eutrophication and salinization. This research explores the integration of hydrothermal carbonization (HTC) and pyrolysis as a potential solution for digestate management, emphasizing volume reduction and energy recovery. The study specifically focuses on the production of biochar from agricultural waste digestate (AWD) in an energy-efficient manner. Utilizing HTC as a pretreatment was found to enhance the heating value of both the AWD and the subsequent pyrolytic char, and it also improved the carbonization degree of the resulting char. Energy balance analysis revealed that the pyrolysis of AWD shifted from an endothermic to an exothermic reaction upon HTC pretreatment. This transition decreased the reaction's energy absorption from 41.1 to 1557.6 MJ to an energy release of 685.1 to 960.6 MJ per ton of digestate, thereby optimizing energy consumption in digestate management. Additionally, it was noted that using acetone as a solvent in gas chromatography for biooil samples with high ammonia content led to the formation of diacetoneamine, an outcome that is deemed undesirable.

1. Introduction

Biodegradable waste, predominantly comprises agricultural waste, the organic portion of municipal solid waste (MSW), food industry residues, and wastewater treatment sludge, among others (Van et al., 2020; Vujovic et al., 2020). Global production of biodegradable waste is estimated to be approximately 150 billion tonnes for agricultural waste (Elbasiouny et al., Springer, 2020), 1.3 billion tonnes for food waste

(Alexandropoulou et al., 2018), 2 billion tonnes for MSW (Chen et al., 2020), and 125 million tonnes for sewage sludge (Vaithyanathan and Cabana, 2021).

Anaerobic digestion facilitates the production of biogas from organic materials and reduces waste volume, making it an optimal process for recycling energy from biodegradable waste (Van et al., 2020). The remaining solid residue, commonly referred to as digestate, typically constitutes about 50% of the feedstock (Gontard et al., 2018).

* Corresponding author. 159 Longpan Road, Nanjing, Jiangsu, China.

** Corresponding author. 9 Engineering Drive 1, #07-26, 117575 Singapore.

E-mail addresses: shule@njfu.edu.cn (S. Wang), yuming@nus.edu.sg (Y. Wen).

¹ These authors contributed equally to this work.

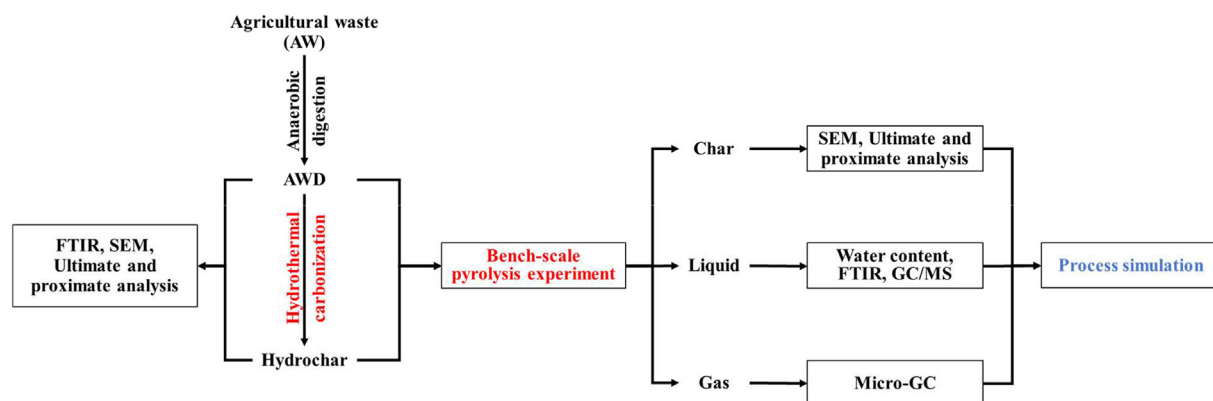


Fig. 1. The raw materials and the proposed methodologies used in this study.

Thermochemical approaches (such as combustion) are conventional for anaerobic digestate disposal. However, the combustion may be limited as environmental policies and technologies change in different countries. In Austria, according to the Austrian Waste Management Act 2002 (BGBl. I No.102/2002 i.d.F. BGBl. I No. 44/2018), digestate from bio-waste (animal by-products of category 2 and 3, separately collected bio-waste, etc.) is considered waste until proper recovery on the soil (Stürmer et al., 2020). And the combustion of anaerobic digestate can lead to a CO₂ tax of EUR 8 per tonne (Sarah Ettlinger, *Eunomia*, 2022). A similar tax on combustion exists in countries such as Norway, Sweden, and the Netherlands (European Environment Agency, 2023; *Plastic Smart Cities*, 2023; *The Norwegian Tax Administration*, 2023). On the other hand, anaerobic digestate is commonly regarded for its potential use in agriculture as a soil conditioner and fertilizer (Gardoni and Guarino, 2016; Nkoa, 2014). However, the vast quantity of digestate generated has surpassed the land's carrying capacity. At present, the use of digestate derived from anaerobic digestion has not been specifically regulated by the European Community and only local regulations have been proposed, with the exception of the application of Good Agricultural Practices, as well as the European "Nitrate Directive" (91/676/EEC) that strongly limits the amount of zootechnical nitrogen that can be applied per hectare of agricultural soil (Nkoa, 2014). For example, in Austria, according to the Austrian Fertilizer Ordinance, the anaerobic digestate must meet the requirement outlined in the Water Act 1959 (BGBl. No. 215/1959), the Nitrate Action Programme Directive (BGBl. II No. 385/2017) and the soil protection laws of the Federal States (Stürmer et al., 2020). Beyond the EU, in Scotland, anaerobic digestates are required to conform to BSI PAS110:2014 standards when employed as soil conditioners or fertilizers (Scottish Environment Protection Agency, 2017). In Canada, the use of digestate as an agricultural fertilizer must follow the provisions of the Fertilizer Act and the local regulations (for instance, M.R 37/2016 Waste Management Facilities Regulation and Nutrient Management Regulation in Manitoba) (Canadian Bioenergy Association, 2019). Consequently, it is advisable to devise more sustainable waste management methods for digestate (Dutta et al., 2021). For these reasons, many industries engaged in the digestion of organic waste are compelled to either dispose of their digestate (in landfills or municipal solid waste incinerators) or subject it to post-treatment, which results in a substantial economic impact (Gardoni and Guarino, 2016).

Pyrolysis is a thermal decomposition process of organic materials in an oxygen-free environment, resulting in various products such as char, bio-oil, and gases (Fu et al., 2022). It is particularly efficient for agricultural waste digestate (AWD) and other organic waste, facilitating harm reduction, resource utilization, and waste minimization while enable waste conversion into multiple type of recyclable energy and materials. Recently, there has been a growing interest in the potential of digestate pyrolysis. Past research has explored the pyrolysis performances of digestates derived from food waste (Liu et al., 2020; Opatokun

et al., 2015; Yang et al., 2020), roadside grass (Bedoic et al., 2019), sewage sludge (González-Arias et al., 2020), algae (Wahab et al., 2022), agricultural waste (AW) (Vuppaladadiyam et al., 2019; Wang et al., 2022), organic fraction of municipal solid waste (Wen et al., 2021), etc. A significant challenge in using pyrolysis as approach for digestate management is the high-water content of digestate, which hinders its transportation and thermal conversion potential.

Recent studies have investigated the use of hydrothermal carbonization (HTC) as a pretreatment method, in combination with mechanical dewatering and conventional thermal treatment, for managing digestate. HTC is a thermochemical process that transforms organic feedstocks into carbon-rich solids, namely hydrochar, typically at temperatures ranging from 180 to 250°C (Lachos-Perez et al., 2022). This process can reduce the ratio of hydrophilic to hydrophobic groups on the surface of materials (Lin et al., 2022), subsequently enhancing the efficiency of subsequent dewatering processes, such as mechanical dewatering (Pawlak-Kruczek et al., 2020a). It has been confirmed that the application of HTC, in conjunction with the mechanical dewatering process, is more energy-efficient than employing the conventional thermal drying process to manage the water content of digestate (Zhao et al., American Chemical Society, 2014). Utilizing the HTC process for digestate pretreatment holds the potential to facilitate improved overall digestate management (Pawlak-Kruczek et al., 2020b). The combination of HTC and pyrolysis presents a promising strategy to mitigate the substantial energy demands associated with water evaporation from digestate. Concurrently, this approach facilitates the generation of valuable by-products from the digestate.

Garlapalli et al. and Olszewski et al. (2011) conducted comparative analyses of the chars produced from the pyrolysis of AWD, spent grains, and their respective hydrochars (Garlapalli et al., 2016; Olszewski et al., 2020). However, studies investigating the impact of HTC pretreatment on pyrolysis behavior are relatively scarce. Given the potential of combining HTC with pyrolysis for digestate management, a comprehensive study characterizing all pyro-products of digestate and its hydrochar is warranted. This would involve a detailed analysis of the properties and composition of the resulting pyro-products, which is crucial for understanding the implications of this combined treatment approach for waste management and potential applications of the resulting products.

The total energy potential of the produced agricultural waste significantly surpasses that of other biodegradable wastes (Gontard et al., 2018); hence its selection as the raw material for this study. Pyrolysis experiments of AWD and its HTC pretreated hydrochar were conducted at the bench scale under varying temperature conditions. These experiments included an in-depth analysis, covering both energy and mass balance evaluations as well as characterizations of the pyrolysis products. To our knowledge, this study is the first to comprehensively demonstrate the feasibility of digestate management through an integrated process that combines HTC and pyrolysis.

2. Materials and methods

The methodology employed in this study is depicted in Fig. 1. This study encompasses bench-scale pyrolysis experiments conducted on AWD and its resultant hydrochar. A thorough characterization was performed using scanning electron microscopy (SEM), ultimate and proximate analyses, and Fourier-transform infrared spectroscopy (FTIR) to evaluate the hydrochar and char. Additionally, gas chromatography-mass spectrometry (GC/MS) and FTIR were utilized to analyze the functional groups present in liquid organics. The water content and gas components were ascertained via Karl Fischer Titration and Micro-Gas Chromatography (Micro-GC), respectively. The characterization results were instrumental in informing process simulations, thereby facilitating a comprehensive understanding of the pyrolysis products generated.

2.1. Raw materials

The initial substances and the process of preparing the materials are identical to those employed in a prior investigation (Wang et al., 2022). Succinctly, the primary origin of the initial agricultural waste was bovine feces. This waste underwent anaerobic digestion at an agricultural biogas facility located in the Silesia region of Poland. The resulting AWD was gathered from the exit of the anaerobic digestion reactor.

2.2. Bench-scale experiments

The production of hydrochar involved subjecting the generated AWD to HTC at a temperature of 190°C for a duration of 30 min within an autoclave vessel. This vessel was outfitted with an external heating mantle, which consisted of multiple electric heating tapes wrapped around its exterior. Following the HTC process, a colander and a clean cotton cloth were utilized to separate the effluent from the hydrochar. The extracted material was then left to drain for a period of 20 min to remove any remaining effluent. A more comprehensive description of the HTC process setup is available in other literature (Wang et al., 2022).

Subsequently, the resulting AWD and hydrochar were dried in an oven at a temperature of 110°C for a total of 24 h. After this initial drying phase, the samples were pulverized and sieved to achieve a particle size of less than 1 mm in diameter. Following the sieving process, the particle samples underwent a second drying period of 24 h at a temperature of 100°C.

The configuration of the bench-scale pyrolysis experiments is illustrated in Fig. 2. This study involved storing approximately 30 g of AWD or its hydrochar in a crucible. A thermocouple, positioned within the reactor, continuously monitored the feedstock temperatures throughout the experiment. Nitrogen gas was infused into the entire system at a flow rate of 200 mL per minute. The cooling system comprised a condenser and two gas washing bottles set at -20°C, a two-necked flask at room temperature. Following the experiment, the resultant char was retrieved from the crucible. The cooling system captured the condensable vapors, which were then collected as liquid products. Meanwhile, the permanent gases were directed through a Micro-Gas Chromatograph (Micro-GC) before being stored in the gas bag, ensuring the complete collection of all pyro-gases before the experiment's conclusion.

2.3. Characterization of raw materials and pyro-products

The ultimate and proximate analyses, ash compositions, and carbohydrate contents of the AWD and its hydrochar were characterized and have been reported in a previous study (Wang et al., 2022). The methods applied are listed in Table S1, and the corresponding results are provided in Tables S2 and S3. The elemental compositions (carbon, hydrogen, nitrogen, sulfur and oxygen content) of the produced chars were determined using an organic elemental analyzer, vario EL cube (Elementar Analysensysteme GmbH, Germany). The morphologies of the AWD, hydrochar, and produced char were characterized using a Scanning Electron Microscope (SEM, Hitachi S3700 N) with a secondary electron (SE) imaging mode. The operating voltage was set at 15 kV. The powder of each sample was prepared and placed on a conductive carbon adhesive tape before observation.

The liquids product contained two phases: an aqueous phase and heavy organics phase. These were separated by simply pouring out the

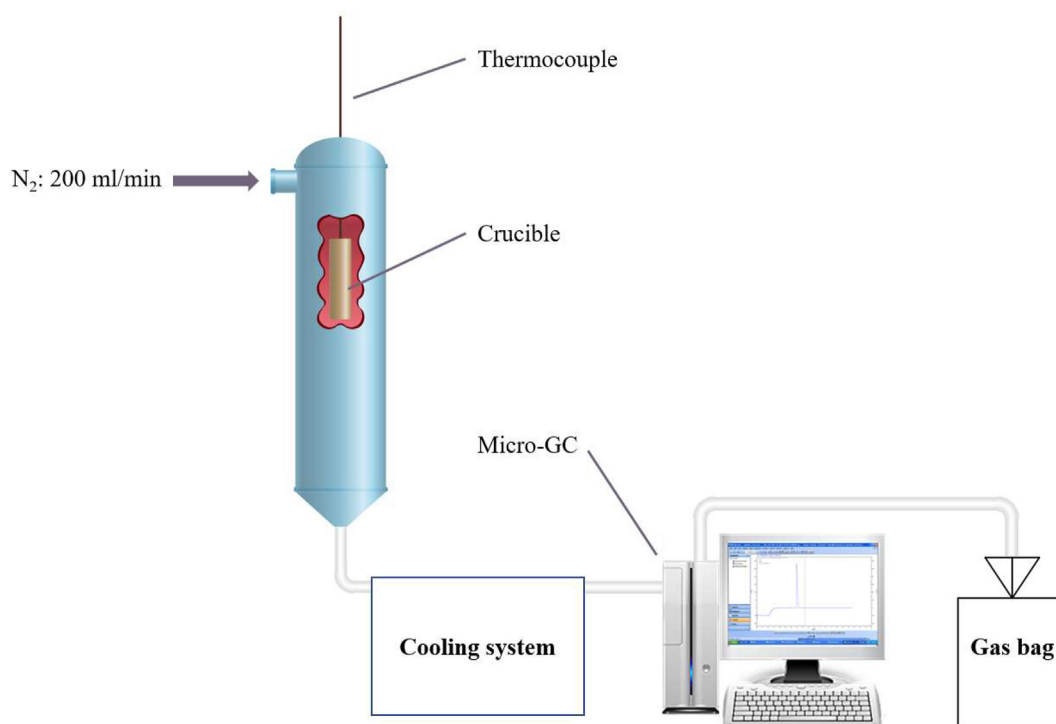


Fig. 2. The schematic of the setup of bench-scale pyrolysis experiments.

Table 1
Mass percentage of pyrolysis of AWD and its hydrochar at 450, 550, and 650°C.

	Char (%)	Heavy organics (%)	Light organics (%)	Reaction water (%)	Gas (%)
AWD 450	44.01	16.74	5.62	10.29	16.93
AWD 550	42.53	19.08	4.99	9.91	17.75
AWD 650	39.88	23.40	4.19	8.69	21.55
Hydrochar 450	44.11	16.91	7.63	15.37	14.43
Hydrochar 550	43.75	16.60	6.87	13.58	16.94
Hydrochar 650	42.23	16.78	6.26	11.77	17.84

aqueous phase from the condenser and gas-washing bottles, leaving the heavy organics adhered to the inner surface of the condenser and gas-washing bottles. Methanol and acetone were used as solvents to dissolve the heavy organics for collection. The water content of the collected aqueous phase was determined using the standard method ASTM E203. The water content in the aqueous phase is referred to as 'reaction water' in this study, and the corresponding organics in the aqueous phase are referred to as 'light organics'. The produced liquid samples were first dissolved in methanol and then characterized using a Gas Chromatography/Mass Spectrometry (GC/MS) system. The GC used was an Agilent 7890A with an Agilent DB-1701 GC column, and the combined MS was an Agilent 5975C. The GC/MS oven program was initially set to 70°C and held for 10 min once sample was injected, then increased to 280°C at a heating rate of 3 °C/min, held for 20 min. An Agilent 490 micro-GC was used to determine the compositions of the produced gases. The contents of H₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ were characterized.

2.4. Analysis of energy flows

A comprehensive analysis of the energy dynamics involved in the pyrolysis of AWD and hydrochar was performed using Aspen Plus V12.1 simulation software. For the purpose of this research, both AWD and hydrochar were categorized as unconventional compounds and were simulated using the HCOALGEN and DCOALIGT models for their physical and chemical properties, respectively. The UNIQUAC physical property method was applied to predict the thermodynamic properties and phase equilibria of the feedstock and product mixtures. The energy required for pyrolysis was defined as the heat needed to increase the feedstock temperature from ambient room temperature to the target pyrolysis temperature. This parameter is crucial for comprehending the energy requirements of the pyrolysis process and facilitates the

calculation of the system's overall energy efficiency. To compute the reaction heat, the energy input of the feedstock was contrasted with the energy output of the products. The disparity between these two quantities signifies the net energy alteration associated with the pyrolysis process.

3. Results and discussion

3.1. Mass balance

The results of the mass balance of pyrolysis products of AWD and hydrochar at temperatures of 450, 550, and 650°C are presented in Table 1. The total values for each case fall within an acceptable range of 93.59%~98.45%. This variation is attributed to the thermal decomposition of organic materials, which occurs within this temperature range. Specifically, char yields exhibit a negative correlation with temperature, whereas gas yields display the opposite trend. Throughout the experiment, hydrochar demonstrated lower temperature sensitivity compared to AWD, which was attributed to the decomposition of cellulose and hemicellulose during HTC treatment. Thereafter, the hydrochar matrix contains a higher lignin content and a more carbonized structure than that of AWD. The yields of aqueous phases (light organics and reaction water) produced during the pyrolysis of AWD or its hydrochar are inversely related to temperature. This suggests that light organics degrade into smaller gas molecules as the temperature increases. Conversely, as the temperature rose from 450 to 650°C, the yield of heavy organics from AWD pyrolysis increased from 16.74% to 23.40%, while that of hydrochar pyrolysis remained relatively constant at approximately 16.7%. This discrepancy may be due to a higher carbonization degree of matrix of hydrochar than it of AWD, which increases the thermal stability of hydrochar. Notably, HTC pretreatment markedly enhances oxygen removal as reaction water, also minimizes the production of oxygen-containing gases.

3.2. AWD, hydrochar, and their chars

The FTIR spectra of AWD and its hydrochar are illustrated in Fig. 3 where the identified peaks and their associated functional groups are indicated. The observed bands at 1030 cm⁻¹ (corresponding to -C-O-R, -Si-O), 2850 cm⁻¹ (symmetric -C-H), 2925 cm⁻¹ (asymmetric -C-H), and the range from 3000 to 3600 cm⁻¹ (associated with -OH and amine groups) were consistent with FTIR peaks reported in previous studies on sewage sludge (He et al., 2013), poplar leaves (Yu et al., 2022),

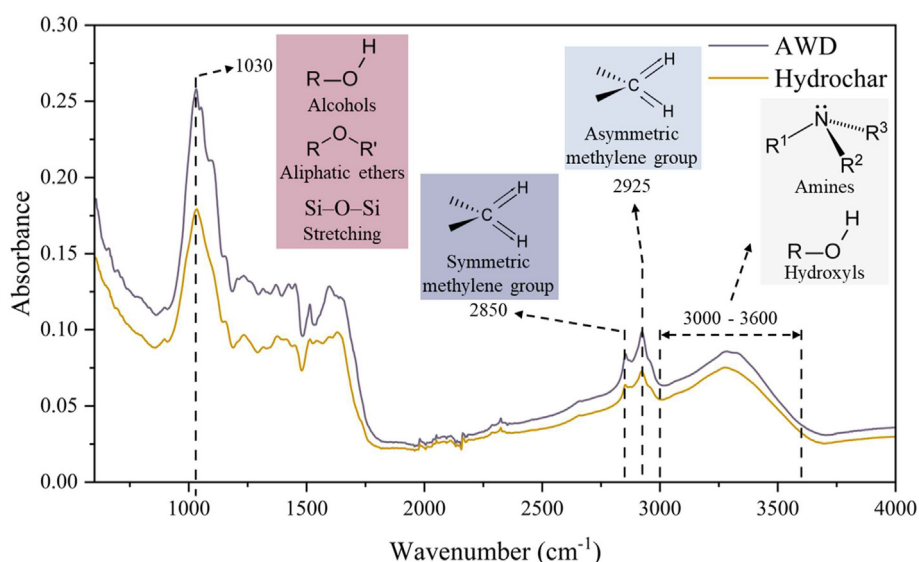


Fig. 3. FTIR spectra of AWD and its hydrochar.

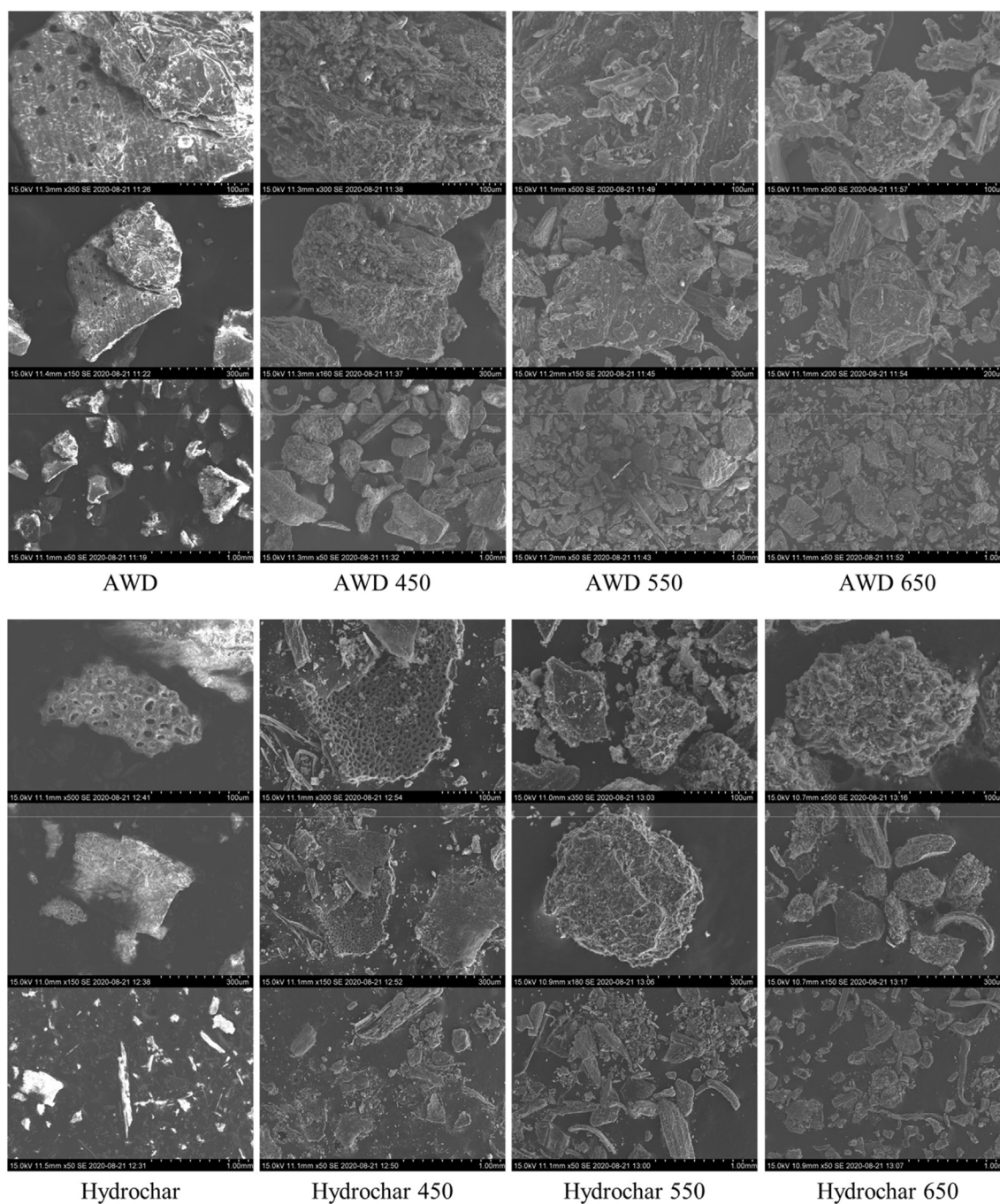


Fig. 4. SEM images of AWD, hydrochar, and their chars produced at 450, 550, and 650°C.

macroalgae (Xu et al., 2013), etc. The pronounced intensity of the band at 1030 cm^{-1} correlated with the high silicon dioxide contents (Table S3) in both the AWD and its hydrochar. Notably, the hydrochar exhibited a FTIR curve analogous to that of the AWD, albeit with a diminished intensity, particularly at 1030 cm^{-1} (associated with oxygen-containing functional groups). This reduction in intensity is attributed to the polymerization reactions occurring on the surface of the feedstocks during the HTC pretreatment process.

The morphology of AWD, hydrochar, and the resulting chars was analyzed by using SEM (as depicted in Fig. 4). A comparative analysis of the SEM images of AWD and its corresponding hydrochar indicates that the hydrochar possesses a more porous structure compared to the AWD. This enhanced porosity can be ascribed to the decomposition of organics during the HTC process (Wang et al., 2018), a phenomenon previously

documented in a study utilizing sewage sludge as the raw material (Gai et al., 2016). Moreover, it is noticeable that the char produced at higher pyrolytic temperatures is more fragmented. Specifically, the char obtained from hydrochar at 450°C displays a pronounced porous structure (Fig. 5. Hydrochar 450) whereas the others do not exhibit this characteristic. This observation aligns with a prior study, which confirmed that chars derived from hydrochar exhibit greater porosity than those obtained from the original raw materials (Hu et al., 2014). However, it is important to note that existing pores may be compromised as the pyrolytic temperature escalates (Hu et al., 2014).

The results of the elemental analysis of the chars produced at varying temperatures are presented in Table 2 alongside the elemental composition of their respective raw materials. It is evident that as the pyrolytic temperature increased from 450 to 650°C, there was a notable decrease

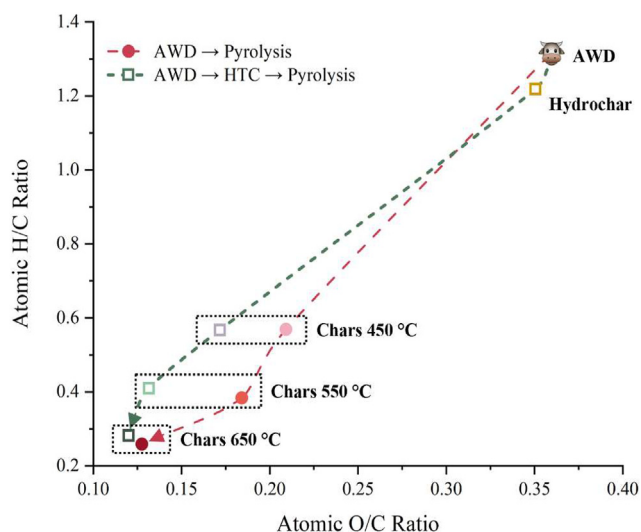


Fig. 5. Van Krevelen diagram which contains the AWD, hydrochar, and their produced chars.

Table 2

Elemental analysis results of AWD, hydrochar, and the produced chars (in dry basis).

	C (%)	H (%)	N (%)	S (%)	O ^a (%)	Ash (%)
AWD	50.00	5.500	4.99	0.700	23.88	14.20
AWD 450	52.06	2.485	3.76	0.198	14.51	26.99
AWD 550	51.65	1.663	3.33	0.209	12.67	30.49
AWD 650	54.61	1.186	3.03	0.213	9.28	31.68
Hydrochar	52.80	5.400	4.31	0.390	24.66	12.20
Hydrochar 450	57.72	2.748	4.23	0.182	13.21	21.91
Hydrochar 550	58.93	2.025	3.97	0.173	10.33	24.58
Hydrochar 650	59.86	1.417	3.35	0.181	9.57	25.62

^a Calculated by difference.

in the content of hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O), attributed to the thermal decomposition and subsequent volatilization of organic matter (Guizani et al., 2017). Consequently, the loss of organic content led to an increase in the ash content of the AWD and hydrochar, from 14.20% and 12.20%, to 31.68% and 25.62%, respectively. Additionally, the carbon (C) content of the hydrochar increased from 52.80% to 59.86%. To assess the degree of carbonization, the atomic ratios of H/C and O/C can be utilized.

The Van Krevelen diagram is a useful tool for visually representing the atomic ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) in feedstock (Wen et al., 2021). Fig. 6 illustrates the positions of AWD, hydrochar, and the produced chars on the Van Krevelen diagram. It is evident that as the pyrolysis temperature increased from 450 to 650 °C, the degrees of carbonization of AWD and hydrochar increased, as indicated by the decrease in atomic H/C and O/C ratios. Specifically, the HTC process slightly reduced the atomic H/C and O/C ratios of AWD from 1.31% and 0.36% to 1.22% and 0.35%, respectively. These findings are consistent with several previous studies (Cao et al., 2019; Zhang et al., 2014). Interestingly, employing HTC as a pretreatment significantly reduced the atomic O/C ratios of the produced chars in the pyrolysis temperature range of 450–550 °C, as depicted in Fig. 5. However, at a pyrolysis temperature of 650 °C, the high carbonization degrees of both AWD and hydrochar resulted in similar atomic H/C and O/C ratios. This observation suggests that the chars derived from hydrochar exhibit a higher degree of carbonization and a lower O/C ratio, indicative of superior fuel properties.

The results highlight the effectiveness of HTC as a pretreatment method in enhancing the fuel properties of chars produced from AWD and hydrochar. The reduction in atomic O/C ratios is particularly

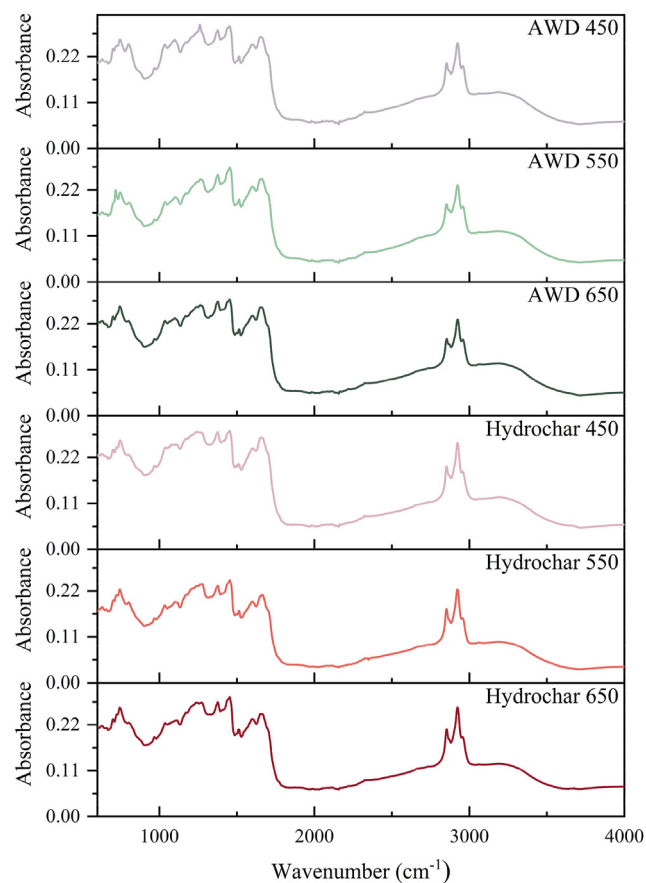


Fig. 6. FTIR results of the liquids yielded from pyrolysis of AWD and its hydrochar at 450, 550, and 650 °C.

significant as it is directly related to the fuel quality of the produced chars. A lower O/C ratio is associated with higher energy content and better combustion characteristics, which are crucial for the efficient utilization of char as a renewable energy source. Furthermore, the lower O/C ratios observed in char derived from hydrochar pyrolysis, as compared to that from AWD, can be attributed to the increased removal of oxygen in the form of water. This observation may serve as an indication that HTC pretreatment alters the oxygen composition in the feedstock, making it more conducive to water generation rather than carbon oxides (CO_x).

3.3. Liquids

The FTIR results of the obtained liquids are illustrated in Fig. 6. FTIR is a valuable technique for identifying the functional groups present in bio-oil, thereby providing crucial information (Ding et al., 2021; Xiu et al., 2010). As depicted in Fig. 6 all six liquids exhibit analogous peaks at 748 cm⁻¹ (aromatic group), 1265 cm⁻¹ (alkyl aryl ether), 1374 cm⁻¹ (nitro compounds), 1453 cm⁻¹ (cyclic aromatic), 1601 cm⁻¹ (amide), 1663 cm⁻¹ (carboxylic acids and esters), and 2924 cm⁻¹ (hydrocarbons) (Martins-Vieira et al., 2023; Sardi et al., 2023), respectively. The aromatic structure could be derived from the degradation of lignin and the polymerization of light organic components, while the amide and other nitrogen-containing compounds could result from the pyrolysis of proteins originating from the cow's digestive system or the anaerobic digestion process. Other small oxygenates result from the pyrolysis of carbohydrate components, such as cellulose, hemicellulose, and other sugars. Similar FTIR results are found from the bio-oil produced from the pyrolysis of microalgae (Sardi et al., 2023). It is challenging to compare the FTIR results between different cases; therefore, a GCMS

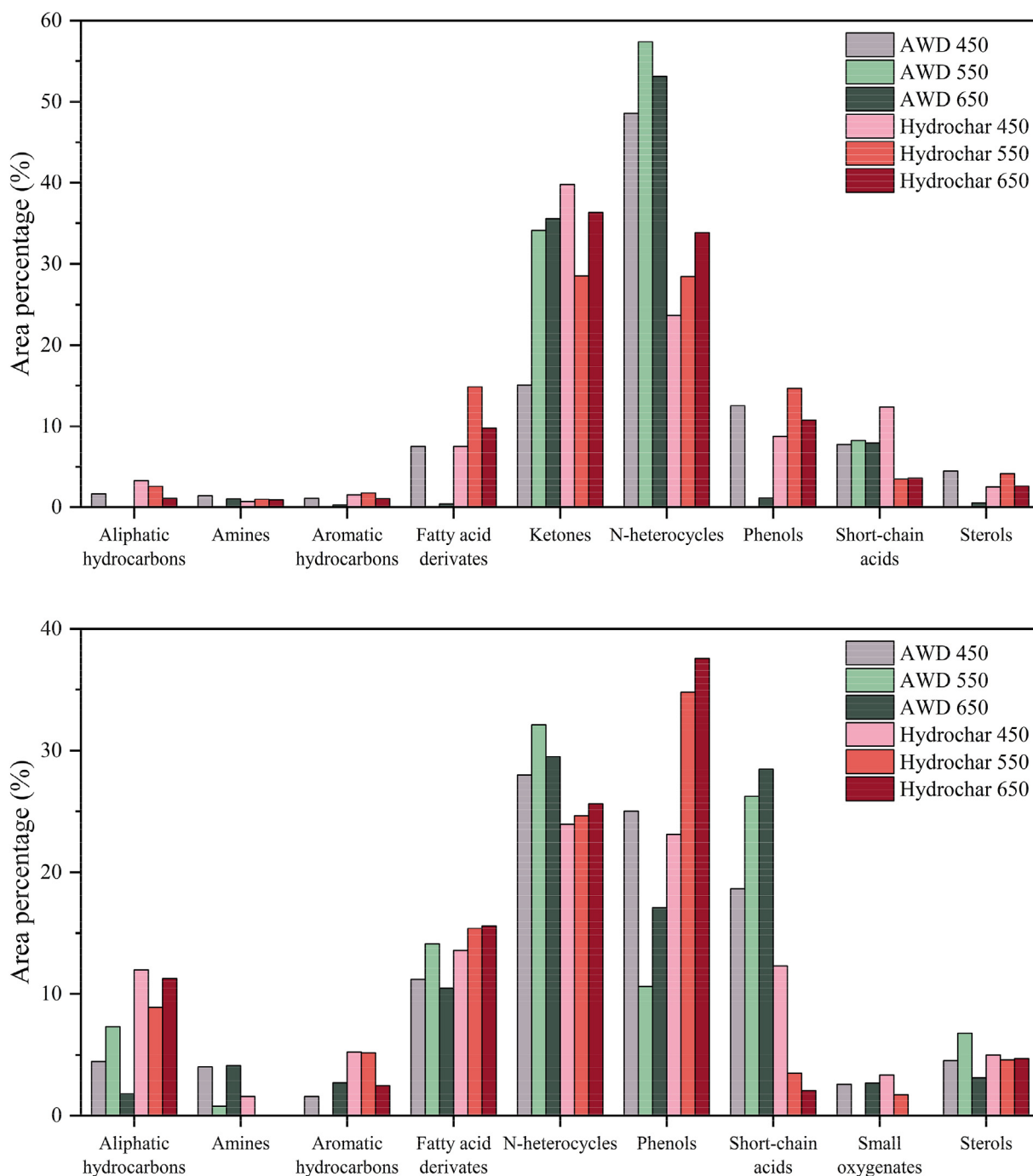


Fig. 7. The GC/MS results of liquid product by using acetone (upper) and methanol (lower) as solvent, respectively.

test was conducted for a more detailed analysis of the liquid components.

The liquid product obtained from the process being studied is characterized by heavy, viscous oil fractions with complex molecular structures. To facilitate the GC/MS analysis of these components, the liquid product was diluted with two different solvents, acetone and methanol, to compare their efficacies. The data obtained is illustrated in Fig. 7, showing a significant disparity between the two solvent conditions. When acetone was used as the solvent, the GC/MS analysis showed a relatively weaker signal for several chemical species, including aliphatic hydrocarbons, amines, fatty acid derivatives, and aromatic hydrocarbons, compared to the stronger signals observed when methanol was used. Additionally, the acetone dilution showed a distinctly different

trend in temperature change for other components compared to the methanol dilution. A notable observation in the acetone-based analysis was the prominence of diacetonamine, which appeared as a strong signal but was conspicuously absent in the methanol-based results (refer to the ketones peak in Fig. 7). This phenomenon could potentially be attributed to the interaction between acetone and ammonia compounds, resulting in the formation of diacetonamine (Bradbury et al., 1947). The significant differences between the results obtained using acetone and methanol as solvents for the liquid product dilution highlight the importance of selecting an appropriate solvent for the analysis of nitrogen-rich feedstocks. As demonstrated in this study, acetone may not be the most suitable choice due to its potential reactivity with ammonia compounds and the subsequent formation of diacetonamine.

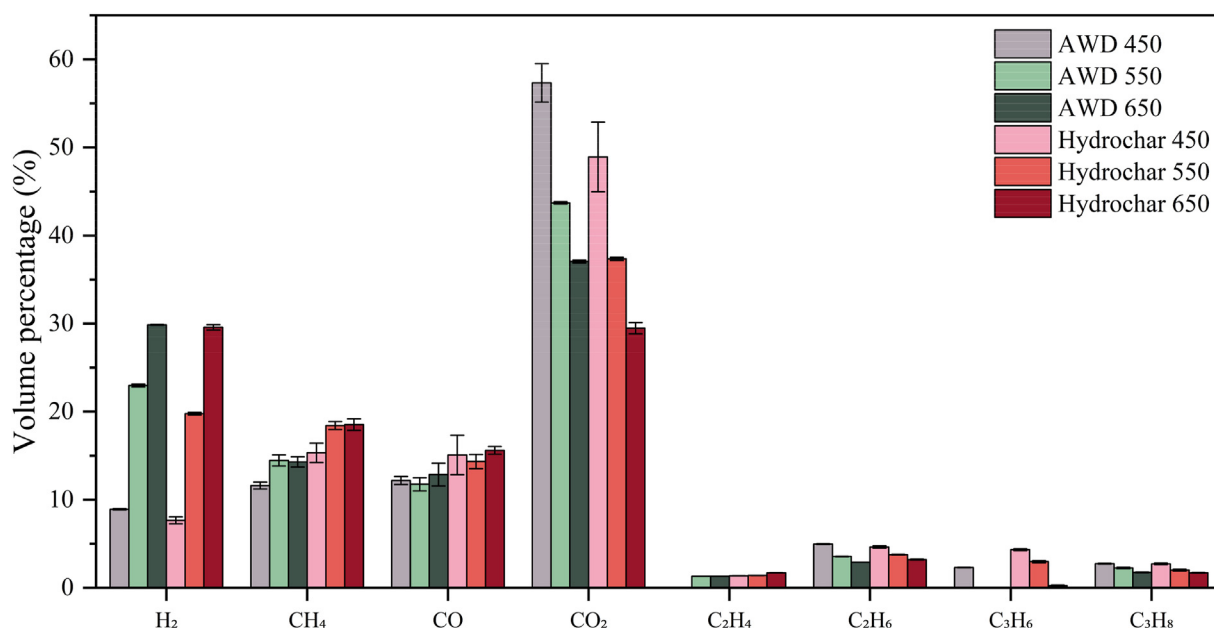


Fig. 8. Gas yield rates of pyrolysis of AWD and its hydrochar at 450, 550, and 650 °C.

According to the results obtained from GC/MS using methanol as a solvent, the HTC pretreatment led to an increase in the abundance of aliphatic hydrocarbons and aromatics in heavy organics, while simultaneously decreasing the nitrogen-containing components and carboxylic acids. This phenomenon can be attributed to the degradation of cellulose and hemicellulose during the HTC pretreatment process. Specifically, nitrogen-containing compounds such as protein has the ability to be partially hydrolyzed then dissolve in the water disposed from the HTC process.

3.4. Gases

Fig. 8 illustrates the volume percentages of the pyro-gases produced. It is evident that the application of HTC pretreatment led to a slight reduction in the volume percentages of H₂ in the pyro-gases produced at 450, 550, and 650 °C, from 8.91%, 22.97%, and 29.86% to 7.66%, 19.76%, and 29.58%, respectively. Conversely, the gases produced from hydrochar exhibited a higher CH₄ content (15.33%~18.53%) and a lower CO₂ content (29.48%~48.92%), indicating superior fuel properties compared to the gas produced from AWD, which contained 11.61%~14.30% CH₄ and 37.05%~57.34% CO₂. The reduced CO₂ concentrations in the pyrolysis gas of hydrochars, compared to untreated AWD pyrolyzed at corresponding temperatures, can be attributed to decarboxylation, a common reaction during the HTC of sewage sludge (Djandja et al., 2021) and biomass in general (Kruse et al., 2013).

3.5. Energy flow

The energy balance results associated with the pyrolysis of AWD and its hydrochar were meticulously analyzed using the Aspen Plus V12.1 simulation software, and the relevant data is illustrated in Fig. 9. The results reveal that AWD pyrolysis is an endothermic reaction, requiring heat absorption, while hydrochar pyrolysis is exothermic, releasing heat. This observation may be attributed to the lower proportion of cellulose and hemicellulose in hydrochar compared to AWD. This is because the pyrolysis of cellulose and hemicellulose is significantly endothermic, whereas the pyrolysis of lignin is exothermic. Table 3 offers a detailed depiction of the energy distribution among the products derived from the pyrolysis of AWD and hydrochar at different temperatures. For AWD pyrolysis, most of the energy is allocated to the organic product, whereas,

during hydrochar pyrolysis, the majority of the energy is found in the char product. This occurrence is linked to the HTC process, which pre-carbonizes the feedstock and partially removes volatile components. Additionally, the energy distribution of the liquid product varied for the two feedstocks: it rose with temperature during AWD pyrolysis, but declined with temperature during hydrochar pyrolysis.

3.6. Discussion

In the present study, the pyrolysis of AWD and its hydrochar was examined. It was observed that HTC pretreatment resulted in a pre-carbonization of the AWD, which had a significant impact on the subsequent pyrolysis process, affecting the thermodynamics of the pyrolysis reaction, the yields of the products, and the characteristics of the products.

The investigation encompasses the identification of functional groups and chemicals present in the liquids derived from the pyrolysis of AWD and its hydrochar. It is crucial to highlight that the analysis indicates that acetone may not be the most suitable solvent for GC/MS analysis of liquid samples containing ammonia compounds. Specifically, the GC/MS analysis revealed weaker signals for various chemical species, including hydrocarbons, amines, fatty acid derivatives, and aromatic hydrocarbons, when acetone was utilized, as opposed to stronger signals observed with methanol. This phenomenon is potentially due to the formation of diacetoneamine, a compound formed when acetone reacts with nitrogen-containing compounds in the biooil. Consequently, it is recommended to refrain from using acetone as a solvent for the analysis of nitrogen-rich oil in subsequent studies.

The observation of morphology and analysis of elements indicate that using HTC as a pretreatment significantly enhances the degree of carbonization of the char derived from AWD pyrolysis. This enhancement occurs because the cellulose and hemicellulose transition from solid to liquid phase during the HTC process, resulting in a reduction of pyrolytic liquid yield. Additionally, the HTC process leads to an increase in a lignin-like fraction, accompanied by the production of more resistant aromatic structured compounds. This, in turn, results in an increase in secondary char derived from pyrolysis and a reduction in gas production (Lucian et al., 2019; Volpe and Fiori, 2017; Volpe et al., 2020). Given that char is the predominant product of AWD pyrolysis, and HTC pretreatment notably amplifies both char yield and its graphitization, the

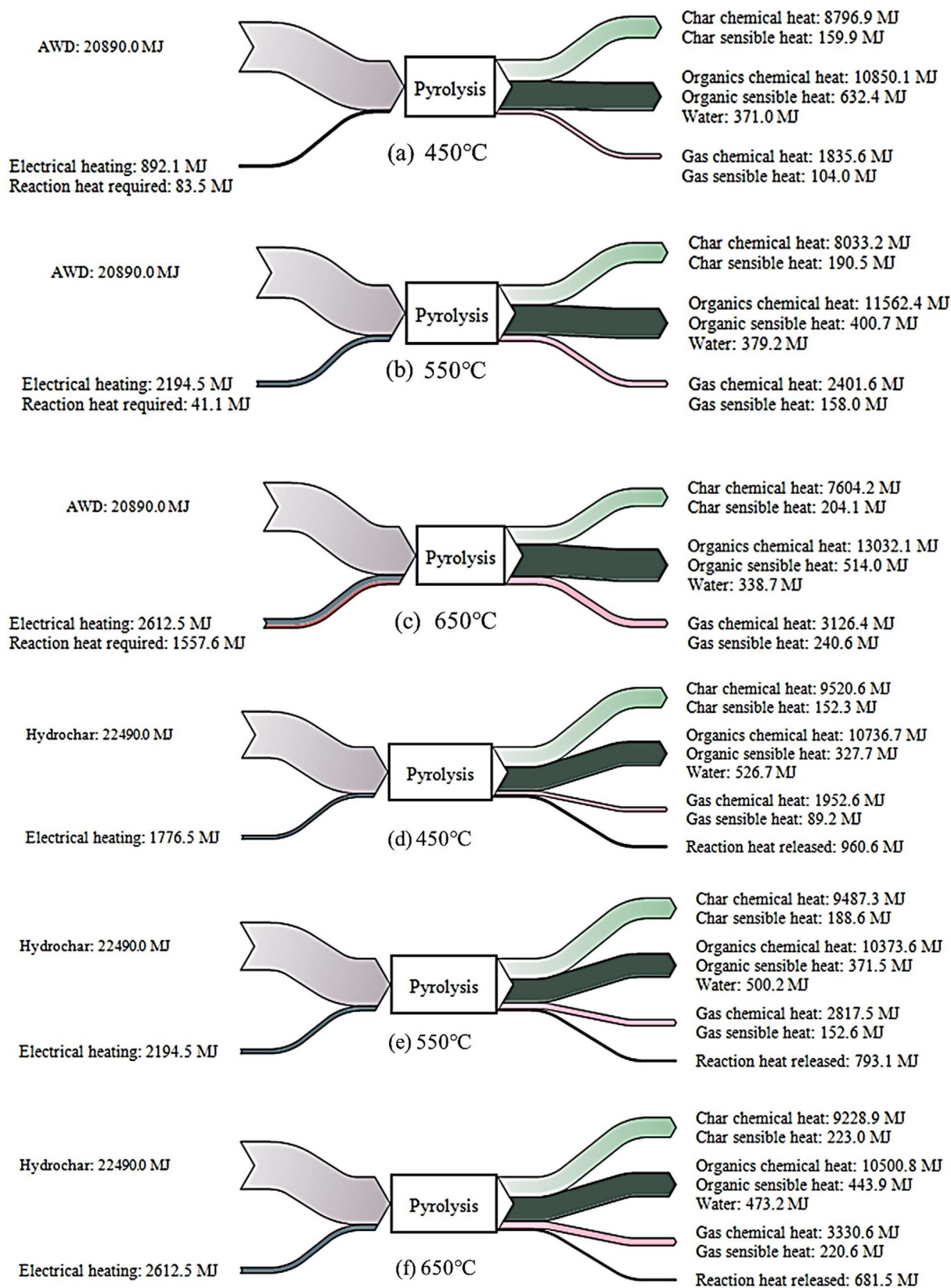
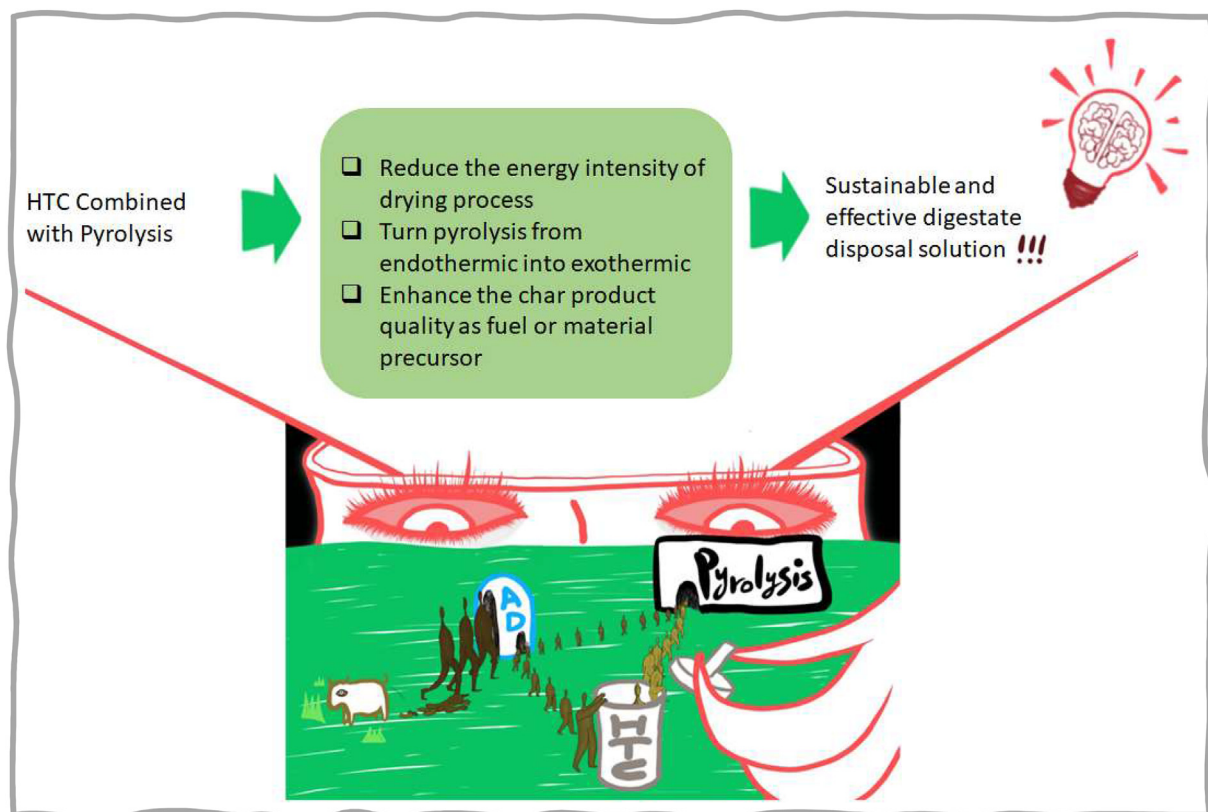


Fig. 9. Energy flows of pyrolysis of 1 ton (a, b, c) AWD and (d, e, f) hydrochar.

Table 3

The total energy distribution in products.

	AWD 450	AWD 550	AWD 650	Hydrochar 450	Hydrochar 550	Hydrochar 650
Char	38.67%	34.74%	30.34%	40.85%	39.71%	37.79%
Gas	8.07%	10.38%	12.48%	8.38%	11.79%	13.64%
Liquid	47.69%	50.00%	52.00%	46.07%	43.42%	43.00%
Sensible and latent heat of product	5.57%	4.88%	5.18%	4.70%	5.08%	5.57%

**Fig. 10.** Summary of the integrated process and characterization of its key attributes.

potential for its utilization in fuel applications or as a precursor for materials is enhanced. Consequently, an integrated HTC-pyrolysis approach may present an efficacious method for biochar production from AWD.

The detailed analysis of energy dynamics in the pyrolysis process indicates that the pyrolysis of AWD is endothermic, while that of its hydrochar is exothermic. This difference can be attributed to the removal of cellulose and hemicellulose from the AWD during the HTC pretreatment. Such findings hint at a potential strategy to decrease the energy requirements of the pyrolysis process, which is conventionally known for its high energy consumption. Fig. 10 provides a comprehensive overview of the integrated process, emphasizing the advancements of the combined method and its prospective applications. By merging the HTC and pyrolysis processes, an innovative approach for digestate management can be established.

4. Conclusions

This research explored the integration of hydrothermal carbonization (HTC) and pyrolysis as a sustainable approach to digestate disposal, aiming to further the principles of a circular economy. The primary findings from this study include:

1. Pretreatment with HTC initiates the carbonization process in digestate, profoundly influencing its subsequent pyrolytic behavior. Such

pretreatment results in a feedstock that possesses enhanced thermal stability, culminating in a higher char yield characterized by a deeper level of carbonization.

2. For the gas chromatography-mass spectrometry (GC/MS) analysis of nitrogen-rich liquid samples, acetone was found to be an inappropriate solvent. This unsuitability is likely attributed to the formation of diacetonamine. Specifically, when acetone was employed for GC/MS analysis of ammonia-abundant liquid samples derived from anaerobic digestion waste (AWD) pyrolysis, it led to the detection of inaccurate signals for several chemical compounds.
3. The pyrolytic reaction of AWD underwent a transition from endothermic to exothermic following HTC pretreatment. This change resulted in a reduction of the reaction's energy absorption, ranging from 41.1 to 1557.6 MJ, to an energy release between 685.1 and 960.6 MJ per ton of digestate. Consequently, this transition optimizes energy utilization in the thermal conversion of digestate when employing an integrated HTC-pyrolysis process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gerr.2023.100034>.

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