Coupling hydrothermal carbonization, ultrasound disruption and microwave disintegration with anaerobic digestion

Ph.D. thesis

By

Mahmood Al Ramahi

Supervisor

Prof. Dr Gábor Keszthelyi-Szabó

Co-supervisor

Prof. Dr. Cecilia Hodúr

Doctoral School of Environmental Sciences

Department of Biosystems Engineering

Faculty of Science and Informatics

University of Szeged

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To My Family

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Abbreviations

AD	Anaerobic digestion
BD	Anaerobic biodegradability
BMP	Biomethane potential
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DDW	Double distilled water
DNA	Deoxyribonucleic Acid
DOC	Dissolved organic carbon
DS	Dairy sludge
EPS	Extracellular Polymeric Substances
EC	Electrical conductivity
FTIR	Fourier transform infrared spectrometry
FU	Functional unit
GC	Gas chromatography
Gs	Gasification
HTC	Hydrothermal carbonization
HRT	Hydraulic retention time
ICP	Inductively coupled plasma spectrometry
LCA	Life cycle assessment

MW	Microwave
SAR	Sodium absorption ratio
SCOD	Soluble chemical oxygen demand
SS	Suspended solids
TN	Total nitrogen
TAN	Total ammonium nitrogen
TC	Total carbon
TDS	Total dissolved solids
TOC	Total organic carbon
TS	Total solids
US	Ultrasound
VS	Volatile solids
VFAs	Volatile fatty acids
WWTP	Wastewater treatment plant

1. Introduction

The efficient treatment of dairy sludge is a challenge due to its high content of proteins, carbohydrates and fats. The relative proportions of these compounds in dairy sludge vary depends on the methods of operation and hence, onsite solutions prior to final disposal are needed and required [1]. Anaerobic digestion (AD) is a biological process in which the organic matter is converted into carbon dioxide (CO_2) and methane (CH_4). AD has been considered previously as an efficient treatment technique for industrial and municipal waste sludge [2]. AD breaks down sludge gel networks and reduce water affinity of sludge throughout the biological series of hydrolysis, acidogenesis, acetogenesis and methanogenesis [3]. However, the high rates of fats, carbohydrates and proteins in dairy sludge limit its conversion rate during AD [4]. Therefore, several studies have dealt with the aspect of coupling the biological treatment (i.e., AD) with several thermochemical processes such as microwave irradiation, hydrothermal carbonization (HTC) and biomass steam gasification to enhance the overall efficiency of AD.

Unlike the conventional heating, heating via microwave (MW) irradiation is converted directly into thermal energy through the molecular interaction with the electromagnetic field. Thus, it is expected to increase the surface area of sludge and improve the enzymatic degradation of the organics [5]. Moreover, MW irradiation is responsible for changing the positioning in the polarized side chains, which results in breakage of the hydrogen bonds, disintegration of the flocs matrix, and changing the protein structures of the microorganisms [6]. Destruction of the microorganisms occurs because of the thermal effect of the MW irradiation. However, several studies argued that MW irradiation has athermal effect [7].

HTC on the other hand is a thermochemical process in which saturated water and vapor pressure are utilized to convert waste biomass into carbon-rich products [8]. HTC is typically performed in temperature ranges between 150–350 °C and autogenous pressure [9]. Hence, the water content stays in the aqueous phase during the HTC reaction, but its density and dielectric constant decrease. Similarly, the O and H contents of the feedstock decrease because of the intense dehydration and decarboxylation reactions taking place during the process [10]. HTC-derived hydrochar can easily be separated from its aqueous phase due to its high hydrophobic and friable properties [8]. Moreover, the high mass and energy density of HTC hydrochar make it suitable as a clean energy source [11].

Steam gasification is another thermochemical technique that converts the dry biomass into syngas and char. In some cases, a non-negligible amount of liquid products is also produced. Syngas is the gaseous mixture containing CO, H_2, CH_4, CO_2, H_2O, and N_2, while char is the solid carbonaceous material with highly porous structure and ash [12]. Similar to HTC, coupling AD with steam gasification has been evaluated previously, but in two approaches only. In the first approach, steam gasification of the AD digestate was evaluated to increase the energy recovery and eliminate its emissions. While in the second approach, the injection of char inside the AD reactor to enhance the reactor performance was investigated [13]. However, the main disadvantage of biomass steam gasification is the energy required for drying the feedstock. Hence, hydrothermal pretreatment of biomass is suggested before steam gasification to enhance the mechanical dewaterability of sludge [14]. In addition, hydrothermal treatment is expected to improve the syngas quality during steam gasification [15]. To the best of our knowledge, there is no study as of yet investigated HTC of AD digestate for the possibility of subsequent steam gasification. Therefore, the feasibility of AD-HTC and AD-MW coupling was investigated and evaluated in this work

The current research considered low HTC and MW processing temperatures, short retention time, and the reuse of the process water for the sustainability of the process. In this respect, the pretreatment of raw dairy sludge and AD digestate was performed at temperatures below 80 °C in case of MW treatment and between 80-240 °C in case of HTC. Then, the produced products were used as an enhancer in the AD and biomass steam gasification. Moreover, the effect of the thermal pretreatment on sludge biodegradability was evaluated based on Boyle's equation. Figure 1 highlights the novelty in the present work by presenting the recently investigated combinations and those assessed herein (objective 1&2).

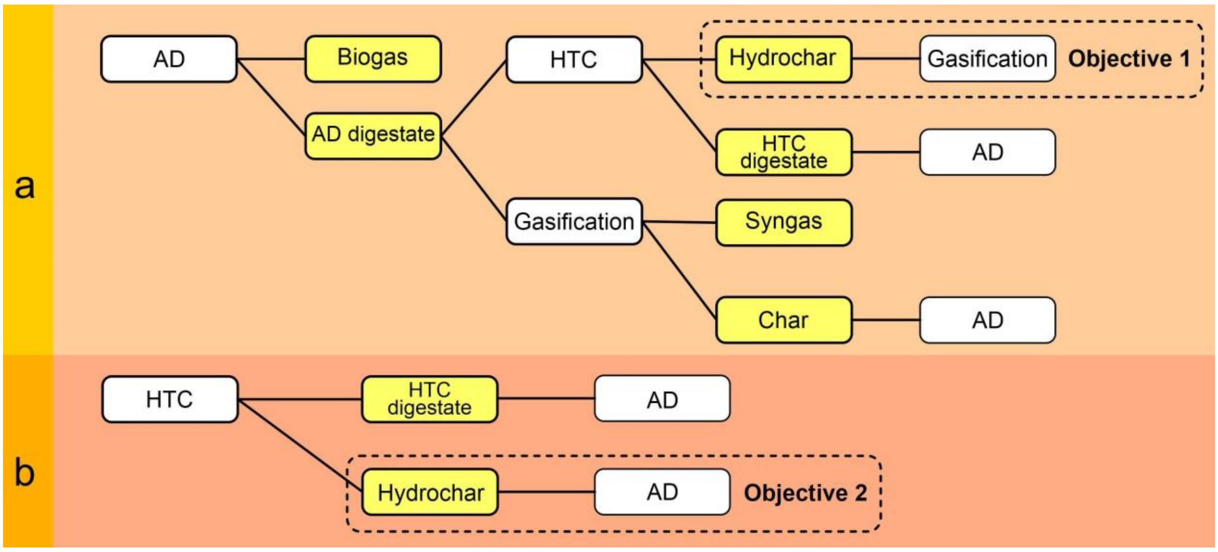

Figure 1. *A schematic diagram representing (1) HTC post-treatment and (2) HTC pretreatment to AD.*

Resource recovery from wastewater treatment plants (WWTPs) is a multi-disciplinary field of study, ranging from energy and nutrient recovery to the production of bio-energy and bio-fertilizers, and other valuable resources. This work attempts to provide a holistic view of the resource recovery within the wastewater treatment domain by analyzing its benefits and contributions. Further, to narrow down the focus and scope of this thesis and conduct a comprehensive research in the field of sustainable energy systems, the implementation of different pre and post treatment techniques to anaerobic digestion were analyzed and evaluated. The choice of studying biogas and hydrochar recovery from WWTPs primarily was inspired by my M.Sc. work at Zuckerberg Institute for Water Research, BGU in Israel.

To conduct quality research and maintain the focus of the thesis, the scope is limited to analyzing energy recovery through biogas, hydrochar and syngas generation. More so, an analysis of all recoverable resources such as nutrients and other inorganic materials were included in the scope of this project. Further, this research tried to analyze the overall sustainability of the WWTPs and examine the various mechanical, chemical, and biological processes that make up the complete wastewater treatment system. However, an in-depth Life Cycle Analysis (LCA) and Material Flow Analysis (MFA) covering the entire WWTP value chain was not possible in this work due to time limitation.

2. Literature review

The need for renewable and sustainable energy alternatives is essential to mitigate the global warming which implies a focus on reducing our waste to a minimum while recovering maximum resources from waste streams, which in turn, will reduce our dependency on fossil fuel [16].

In line with the concepts of sustainable development and circular economy, this research thesis explores the avenues of resource recovery from WWTPs. As essential waste treatment utilities in urban areas, WWTPs present a unique opportunity to recover important resources such as energy and nutrients. This section reviews the potential benefits of energy and resource recovery from WWTPs, and develops an assessment tool for evaluating the technical, economic, and ecological feasibility of recovering energy in the form of biogas and hydrochar. It is aimed at energy and sustainable development of WWTPs operations and provides a tool to assess the potential for recovering biogas and biomass for bioenergy production. This work also evaluates the feasibility of implementing a hydrothermal reactor in combination with anaerobic digestion in a functional WWTP.

The literature review is useful in synthesizing information on important concepts from different aspects, their benefits and limitations, and to identify sectoral knowledge gaps that are common across this research area. This holistic literature review aims to cover the field of resource recovery from wastewater and sludge, and to examine treatment technologies, assessments, research methodologies, case studies, policies, as well as the gaps in the current knowledge.

2.1 Wastewater treatment – global and regional status

Increasing amount of industrial wastewater is discharged every year as a result of human activities. Since the 1980s, an approximate of 10,000 new chemical compounds are introduced to the industrial sector annually. The characteristics of the discharged industrial effluents vary depending on season and collection point. Moreover, industrial effluents vary in their composition depending on the type of the industry, and the materials used. In general, the composition of effluents includes a range of constituents such as biodegradable and non-biodegradable organics, inorganics and inhibitory substances. The differences in the wastewater characteristics in different countries are shown in Table 1 [17].

Table 1. *Industrial wastewater characteristics from different countries around the Globe.*

Parameter (mg/L)	US	France	Hungary	Morocco	Jordan
BOD	110- 400	100- 400	190- 300	45	152
COD	250- 1000	300- 1000	200- 350	200	386
Total solids	100- 350	150-530	250- 400	160	658
TC	319- 419	992-1019	213	144	588
TN	140	340	143	111	419
Total VFAs	944	3003	2218	1002	2010

The industrial effluents may be nutrient deficient and contain high concentrations of heavy metals [18]. The flow pattern of industrial effluent streams is mainly influenced by the nature of operations and it differs by season and location, therefore, a comprehensive understanding of its characterization is essential. The discharged wastewater contains significant amounts of biomass consisting of proteins, carbohydrates and lipids. The specific characteristics of the discharged wastewater vary depending on the methods of operation and hence, the relative proportions of fats, proteins and carbohydrates differ constantly. Some of these compounds result in biodegradability difficulties caused by sludge flotation, which is attributed to the presence of fats [19]. Moreover, the high rate of fat adsorption may limit the transport of soluble substrates and consequently cause the conversion rate in the substrates to decrease [20]. The two common parameters used to investigate the composition of wastewater are the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [21]. BOD is a measure of the amount of the dissolved oxygen consumed by bacteria at 20 °C. While regulations for BOD values vary in different locations, the typical acceptable range must not exceed 300 mg/L [21]. On the other hand, COD is measured chemically by digestion with acids and is used to determine the amount of total organics (including non-biodegradable organics) within the wastewater [22]. COD/BOD ratio has been commonly used as an indicator for the biodegradation assessment of wastewater and its values must not exceed 2.5 for domestic wastewaters and 10 for industrial wastewaters [23].

2.2 Resource recovery potential

There is an essential need to make WWTPs more energy efficient and economically viable. In other words, WWTPs must be designed and operate with resource optimization and energy recovery focus. Netherlands, for example, introduced the concept of 'NEW Factory' which suggests that WWTPs can become factories for recovering 'nutrients, energy, and clean water', and provide a picture of how a sustainable WWTPs can operate in the future [17]. The biorefinery concept envisions WWTPs as factories (refineries) modelled on an oil refinery, where the raw materials (wastewater) are refined to extract and recover several beneficial products, with wastewater treatment being the primary objective. There is also a growing consensus to start looking at WWTPs as wastewater resource recovery facilities where resource recovery is the primary function of the facility, along with wastewater treatment. The value of these resources varies based on their end uses, with the treated water being the most valuable resource that can be recovered from the process [17].

Wastewater sludge is an important carrier of valuable resources such as the water, nitrogen, phosphorous and organic carbon with different proportions (Table 2). The embedded minerals can be utilized in bio-fertilizers, whereas the organic carbon can be used in soil amendment or as a clean energy source [9]. In addition to the recovered water, organic matter and nutrients, the recovered energy can provide an additional value proposition. While several treatment methods require considerable energy during their operation, a net energy gain can be achieved by recovering energy from anaerobic treatment of wastewater and sewage sludge, or through the valorization of bio-fuels using thermo-chemical processes such as hydrothermal carbonization and steam gasification. Anaerobic digestion is defined as the biological process in which a consortium of microorganisms breaks down complex biodegradable organics into methane (50-80%) and carbon dioxide (30-50%) in strict absence of oxygen (anaerobic conditions). The combination of methane and carbon dioxide produced during anaerobic digestion is known as biogas.

Table 2. *Typical properties of the primary and waste activated sludge.*

Parameter (% dry weight)	Primary sludge		Waste activated sludge	
	Typical	Range	Typical	Range
Total dry solids	6- 12	10	2-6	5
Volatile solids	50- 100	85	20- 35	20
N	1.0- 3.5	2.0	0.5- 4.0	1.6
P_2O_5	0.9- 2.9	1.9	2.1-3.0	2.4
K_2O	0-1	0.4	1-3	1
pH	5-8	6	6.5- 7.5	7

Nutrient recovery as biosolids

The capture and reuse of nutrients in agricultural applications from the wastewater treatment process is a common practice [17]. However, only 10-20% of all of the wastewater generated globally is directed into the treatment facilities [17].

Sludge is a concentration of nutrients and organics has a high potential for energy and nutrient recovery. It contains nutrients like phosphorous and nitrogen which are essential for plant growth, giving it the potential use as a fertilizer. The sludge also contain organic carbon that can be used to improve soil structure or produce bio-energy [9]. Relevant policies and legislations were developed to promote sludge utilization which has resulted in increasing use of waste sludge for further applications in agriculture. However, further research into the biochemical effects of sludge use in soil is essential to detect any toxicity or microbial inhibitors before drawing such conclusions [9].

Utilization of sludge differs from country to country based on the local regulations and development priorities. For countries with low soil nutrition like Spain, agricultural use is recommended where nearly 100% of the biosolids are used in agriculture [17]. On the other hand, in heavily industrialized economies, the heavy metals in sludge is a concern, making energy generation from sludge more attractive. This is the case in the Netherlands where almost all of the produced sewage sludge is incinerated for bioenergy production [17]. Thus, it is imperative to separate industrial and domestic wastewaters and limit the concentrations of harmful chemicals and heavy metals in wastewater streams. On a global level, the utilization of waste activated sludge vary from region to another and from country to another. In developing countries such as Turkey, Brazil and Mexico, biosolids are used modestly in agricultural applications, while in other developed nations such as Japan, Austria and the Netherlands, the agricultural uses of sludge is limited due to concerns regarding groundwater pollution [17].

Phosphorous recovery

Phosphorous recovery is becoming more of a necessity than an option, as it is an essential nutrient. The demand for phosphorous will start exceeding the supply by 2035, creating a global challenge for food production and agriculture as there is no substitute available for the nutritional values of phosphorous [17]. Wastewater treatment provide a viable opportunity to recover phosphorous from waste streams, with the potential to replace one third of the global phosphorous demand. Recently, there were some chemical and biological processes introduced to recover phosphorous, with the purpose of using it in agriculture. Such methods included adding magnesium chloride to wastewater streams with high P content in large-scale WWTPs, with several full-scale technology demonstrations across the world [24]. Countries such as Sweden and Switzerland have mandated phosphorous recovery from wastewater treatment plants, and are providing the first experiences in what a regulatory framework necessary to unlock the global potential for phosphorous recovery.

2.3 Energy recovery potential through biofuels

Energy can be recovered from biomass as a solid, liquid or gaseous fuel. In case of solid fuel, biomass quality can be determined by its composition. Specifically, the solid fuel quality can be assessed by plotting its atomic H/C and O/C ratios in the well-known *Van Krevelen diagram* [9]. This evaluation method was established in early literature and is used commonly in solid fuel research.

Based on its reactivity, biomass can be categorized into reactive and inert components. Previous research tried to understand the effect of the reactive and inert components on biomass quality as a solid fuel, including its coking pressure [9,25]. Biomass fuel quality can be improved through hydrothermal treatment during which vitrinite are transformed into devolatilises and then solidifies to form a porous and continuous matrix of metallurgical coke, which acts as a binder to hold other components together [26]. Biomass reactivity during hydrothermal treatment is closely related to the hydrogen content and the carbon molecular structure [27]. A high hydrogen content enhances the mesophase mobility by suppressing the tendency to develop radical molecular species. In summary, biomass characteristic has a significant impact on its combustion behavior if used as a solid fuel to produce bioenergy.

Another possible path in utilizing sludge biomass can be through anaerobic digestion (AD). AD breaks down sludge gel networks and reduce the water affinity of sludge through the biological series of hydrolysis, acidogenesis, acetogenesis and methanogenesis [3]. Hydrolysis is the wet (hydro) disintegration (lysis) of the complex compounds. During hydrolysis, the complex molecules are converted into simpler and more biodegradable forms of organics. Whereas the complex compounds such as carbohydrates, lipids and proteins are converted into sugars, fatty and amino acids, respectively [28]. The second stage of AD is acidogenesis and considered the quickest. In this stage, carbohydrates, amino and fatty acids are broken down into organic acids, hydrogen gas and carbon dioxide by the acidogenic bacteria [29]. The same bacteria convert the resulting organic acids into acetic acids, alongside additional ammonia, hydrogen and carbon dioxide [3]. The final stage of AD is methanogenesis in which methane (CH_4) is produced by the methanogenic microorganisms. Other fermentative products are produced by the methane-forming bacteria. The undigested compounds such as alcohols and organic nitrogen are usually accumulated in the digester and then discharged with the waste activated sludge [30].

In case of pretreatment, higher methane production during AD is a clear indicator of the increased availability of the organic substrates within the biomass, which leads to an enhanced conversion of the organics during methanogenesis (methane production). The amount of methane produced can be expressed in terms of gCOD. The anaerobic biodegradability (BD) of sludge can be calculated based on the experimental results compared to the theoretical results, according to Boyle's Equation (1) [31].

$$BD\ (\%) = (BMP_{exp} / BMP_{th}) \times 100\%. \qquad (1)$$

In all cases, higher theoretical values are expected as Boyle's equation does not account for the non-biodegradable organics. Moreover, not all of the biodegradable organics present in the feedstock are consumed during AD [32].

After the oil crisis in the 70s alongside the growing environmental awareness; biogas utilization took a sharp increase worldwide. Generally; 2 m^3 of biogas can produce energy equal to one liter of diesel [28]. Compared to other renewable energy technologies, biogas is the most practiced worldwide and it has the lowest financial input per unit of energy output compared to other technologies [33]. A typical biodegradation of organics during AD can be represented by Buswell’s Equation (2) [31].

$$C_nH_aO_b + (n - a/4 - b/2)\ H_2O \rightarrow (n/2 + a/8 - b/4)\ CH_4 + (n/2 - a/8 + b/4)\ CO_2 \qquad (2)$$

This theoretical method is derived by balancing the total conversion rate of the organics introduced by CH_4 and CO_2 with H_2O assuming that the composition of the organics is complete. Table (3) shows a typical composition of biogas from different types of feedstock [24].

Table 3. *Biogas composition from different feedstock.*

Feedstock	CH_4 (%)	CO_2 (%)	O_2 (%)	N_2 (%)	H_2S (ppm)
Animal manure	55- 58	37- 41	<1	1- 17	32- 152
Sewage sludge	61-65	36-38	<1	<2	-
Kitchen waste	50-60	34-38	<1	<5	100-900
Agricultural waste	60-75	19-33	<0.5	<1	1000-4000

Ideally, the aim is to enhance the volume of biogas production and the fraction of CH_4, while reducing CO_2 and H_2S. The minimum accepted concentration of CH_4 in biogas for energy production should not fall behind 50% [34].

Anaerobic reactors are classified depending on the phase of digestion, wet or dry. Dry digestion contains approximately 20-40% dry solids, and the wet digestion has less than 15% dry solids. One significant advantage of the dry digestion is that it consumes less water, which reduces the overall volume of the reactor. However, the digestion efficiency is often hampered when the moisture content is not enough, since it decreases the substrate's availability lowering the digestion rates [35]. Another way to classify anaerobic reactors is between batch and continuous reactors. In batch reactors, all stages occur at the same time and in the same compartment. Thus, the hydraulic retention time (HRT) is relatively long and could reach up to 100 days. The main advantages of those systems the simplicity in design and operation, with efficient quality control and low operation cost. Usually, these benefits come at the expense of the variations in the digestion quality [36].

Continuous reactors can be built as single-stage reactor or two-stage reactor. In the latter type, there is spatial separation between the hydrolysis and acidogenic stages from one side, and the methanogensis on the other side for more efficient digestion (i.e. higher biogas generation and shorter HRT). However, these types of reactors are more complex to operate and usually are not suitable for small scale reactors.

Commercially, anaerobic reactors are categorized based on the feedstock and they fall into four general categories according to the American biogas council [29]:

1. Covered anaerobic lagoon digester: Sealed with flexible cover to recover methane and piped to the combustion device. Some systems use a single cell for the combined digestion and storage.

2. Plug flow digester: Long, narrow concrete tank with a rigid or flexible cover. The tank is built partially or fully below grade to limit the demand for supplemental heat. Plug flow digesters are used at dairy operations that collect manure by scraping.

3. Complete mix digester: Enclosed, heated tank with a mechanical, hydraulic, or gas mixing system. Complete mix digesters work best with more dilution of the excreted biomass.

4. Dry Digestion: Upright, silo-style digesters made of concrete and steel with rigid cover. Dry digesters operate at 20 to 42% total solids, which allows them to combine high dry biomass and crop residuals with very dilute liquid biomass or co-substrates.

The specific design of anaerobic reactors depends on the source of waste and the specific purpose. A sustainable organic loading rate (OLR), hydraulic and solids retention time, and the size of the reactor must be considered before designing the reactor in order to get the maximum possible methane yield potential [35]. Moreover, mixing is an important aspect as it helps with dispersion and microbial activities [37].

2.4 Parameters affect biogas production during anaerobic digestion

Since anaerobic digestion consist of microbial processes that are conducted by several groups of microbes in need of different environmental conditions, achieving optimal performance is challenging. In principle, the parameters affect the biological activities might be important for the evaluation and design of any anaerobic digester. The main factors are summarized herein.

pH

pH plays an important role during anaerobic digestion. The optimum range of pH to obtain the maximum biogas production can range between 6.5-7.5 [27]. During the early stages of AD, pH drops with the production of acetate and fatty acids, but methane-forming bacteria consumes those acids and regulate the pH later on. Hence, pH values can serve as an indicator to determine the rates of the processes during anaerobic digestion. For example, in the startup period, the volatile acid production rate is higher than the methane production rate, which can be explained by the lower pH values at the begging of the AD process [30].

Anaerobes are most efficient at a pH range of 5.5-6.5, but the methanogens activity is optimal at a pH range between 6.5-8.2. Therefore, one stage reactors are often less efficient and harder to control than two stage reactors. The latter can compensate the differences in pH between hydrolysis and methanogenesis [38]. The buffer capacity inside the reactor is achieved mainly by the carbonate system and the ammonia produced during the AD process [39].

Temperature

The microbial biological activities accelerate with increasing temperatures, but only to a certain level [40]. This could be attributed to the increased solubility of the organic compounds with increasing temperatures [39]. For example, AD at 20 °C requires twice the retention time compared to that at 40 °C to produce the same amount of biogas [5]. Therefore, AD can perform under ideally under different ranges of temperature between 35°C (mesophilic) and 60 °C (thermophilic) [41]. However, the rates of methanogenesis under thermophilic reactions are higher than those under mesophilic reactions for the same HRT [42]. In summary, methane production can be achieved under a range of temperatures from 0 up to 97 °C [4].

C/N ratio

During AD, C is used for cell growth and energy production, whereas N is consumed to synthesize amino acids, proteins, and nucleic acids. Theoretically, anaerobes consume C 30 times faster than N during AD. Literature recommended an operating C/N ratio between 20/1 and 30/1. Some studies, however, demonstrated that an efficient AD can be accomplished with lower C/N ratio than previously suggested, as low as 10/1 [43]. However, for a successful operation under lower C/N ratio, there is a special need for the development of a specific microbial population and diversity which can be challenging. Improper C/N ratios can result in a high total ammonia nitrogen production resulting in a high volatile fatty acids accumulation and a significant drop in pH [44].

Volatile fatty acids accumulation (VFAs)

Volatile fatty acids (VFAs) are organic acids produced during the first and second stages of AD. VFAs are soluble in water and they serve as substrates for the methane forming anaerobes. VFAs are one of the most important factors controlling the efficiency of AD [45]. The concentrations of VFAs may change during AD because of the change in temperature and the organic content of the substrate [39]. The accumulation of VFAs results in pH drop, however, the methanogenic bacteria balance the acidity of the reactor by producing alkaline products such as ammonium and bicarbonate [39].

2.5 Pretreatment technologies

The efficient treatment of waste sludge is a major challenge because of the high content of proteins, carbohydrates and fats. The relative quantities of these compounds in waste sludge vary according to the change of wastewater components and the variable removal efficiency of the wastewater treatment processes. Some cause biodegradability difficulties related to sludge flotation, which are mainly attributed to high presence of fats. A brief review of some of treatment methods are described herein.

Microwave irradiation

Hydrolysis is the first and could be the rate limiting step during AD [7]. Hence, pretreatment techniques were suggested to facilitate the hydrolysis step during AD to achieve a faster and more efficient disintegration process. Among those, thermal treatment has long been recognized as one of the most effective methods for sludge conditioning. But unlike the conventional heating, heating via microwave (MW) irradiation is converted directly into thermal energy through the molecular interaction with the electromagnetic field. Thus, it is expected to increase the surface area of sludge and improve the enzymatic degradation of the organics [5]. Moreover, MW irradiation is responsible for changing the positioning in the polarized side chains, which results in breakage of the hydrogen bonds, disintegration of the flocs matrix, and changing the protein structures of the microorganisms [39].

Previous studies investigated the effect of MW pretreatment as a function of temperature in which high degrees of sludge solubilization were achieved correlated to high temperatures during MW irradiation. For example, the study of [46] investigated the effect of MW irradiation on waste activated sludge in temperatures between 50–96 °C and concluded an enhancement in biogas production up to 16%. Moreover, the study of [6] reported an enhancement of 50% in biogas production after MW pretreatment in temperatures below 80 °C. However, the prime disadvantage of MW irradiation is its high energy consumption, which can be minimized by combining it with lower energy disruption methods such as ultrasound (US) [47].

Ultrasound (US) disruption

Sludge exposure to US is expected to increase the rate of extracellular polymeric substances (EPS) release and increase the solubility of organics due to the effect of the acoustic cavitation force [47]. The so-called cavitation force is initiated by the energy release upon the implosion of the gas bubbles generated during US treatment. Hence, ultrasound processing is expected to enlarge the reaction boundary and break the bonds of the highly polymeric substances, resulting in more efficient MW disintegration.

Recent studies investigated the combination of MW with other pretreatment techniques such as US to minimize energy consumption. For example, the recent study of [30] investigated the effect of disperser induced microwave pretreatment on the chemical oxygen demand (COD) solubilization. Their results indicated a significant reduction in the energy consumption with an enhanced COD solubilization (22%) and suspended solids (SS) reduction (17%). Another study [48] evaluated the effect of combining alkaline pretreatment with MW irradiation on sludge disintegration during AD and concluded an enhancement of 66% at specific energy input of 38,400 kJ/kg TS. To date, only one study evaluated the effect of ultrasound disruption (US) on MW disintegration of sludge with many research and mythological gaps [29]. Hence, further research and development is needed to understand the effect of this phase separated pretreatment on the energy and resource recovery of the wastewater treatment process, as well as to evaluate its effect on sludge biodegradability as current information is still in its infancy.

Hydrothermal carbonization (HTC)

HTC is a thermochemical process in which saturated water and vapor pressure are utilized to convert waste biomass into carbon-rich products [10]. HTC is typically performed in temperature ranges between 150–350 °C and autogenous pressure [9]. Hence, the water content stays in the aqueous phase during the HTC reaction, but its density and dielectric constant decrease. Similarly, the O and H contents of the feedstock decrease because of the intense dehydration and decarboxylation taking place during the process [10]. In addition to the solid residues, liquid and gas products are also produced during HTC. The liquid products obtained from the HTC of agricultural wastes [49], sewage and dairy sludge [20,50], human excreta [11], and poultry litter [9] have been considered for different purposes, such as the production of nanostructured and adsorbent materials for soil amendment and bioenergy production. The characteristics of HTC products under different ranges of conditions have also been extensively studied [9,20].

HTC-derived hydrochar can easily be separated from its aqueous phase due to its high hydrophobic and friable properties [8]. Moreover, HTC hydrochar has a high mass and energy density and therefore, is suitable for use as a clean energy source [25]. Given its promising attributes, there has been a rapid surge in interest in HTC hydrochar for environmental and renewable energy applications. For instance, [26] highlighted the climate change mitigation potentials of hydrochar, whereas the application of hydrochar for soil amendment has also been well established [51]. The energy conversion and gas emissions during hydrochar production and incineration have also been investigated previously [25,52]. Different approaches have been suggested to utilize HTC hydrochar and liquid products for bio-oil and syngas generation through fractionation and steam gasification [10,53]. Moreover, HTC aqueous phase has been successfully used as a nutrient source for algal biomass production [54].

HTC has also been investigated previously as a post-treatment to AD to reduce the digestate volume and emissions [31], and maximize methane production [55]. However, more information is needed about the energetics of such a coupling to assess its self-sustainability and evaluate the effects of using HTC digestate in soil. Another domain requiring further research is using hydrochar as an enhancer in the AD process [13].

Biomass steam gasification

Steam gasification converts (dry) biomass into syngas and char. In some cases, a non-negligible amount of aqueous phase is also produced. Syngas is the gaseous mixture containing CO, H_2, CH_4, CO_2, H_2O, and N_2, while char is a solid carbonaceous material with a highly porous structure and ash [56]. Similar to HTC, coupling AD with steam gasification has been evaluated previously, but only in two approaches. In the first approach, steam gasification of the AD digestate was evaluated to increase the energy recovery and eliminate its emissions. While in the second approach, the injection of char inside the AD reactor to enhance the reactor performance was investigated [13]. However, the main disadvantage of steam gasification is the energy required for drying the feedstock. Hence, hydrothermal pretreatment of biomass is suggested before steam gasification to enhance the mechanical dewaterability of sludge [57]. Hence, hydrothermal treatment is expected to improve the syngas quality during steam gasification [58].

2.6 Sustainability Assessment

The assessment and selection of different pretreatment processes for energy recovery depends on a variety of decision-making tools and methodologies. The techno-economic-environmental assessments are based on the underlying principles of sustainability, and aim to enable decision-makers to implement processes and pathways that can satisfy the different dimensions of sustainability. Such assessments rely on the definition of adequately list of accepted and relevant criteria and indicators [59].

In this section, different indicators to provide a preliminary understanding of the bioenergy recovery potential from a WWTP are discussed. The technical, economic, and environmental indicators were chosen based on the existing literature.

The assessment methodology

A holistic techno-economic-environmental assessment of bioenegy recovery is dependent on the selection of multi-disciplinary sustainability indicators, which can encompass the different sustainability dimensions. Using these indicators, different tools such as the life cycle assessment (LCA) can be integrated to create a complete techno-economic assessment [20]. In the first phase, the scope of the assessment and the boundaries of the system must be defined. This includes the selection and design of sustainability indicators for the energy recovery systems, the definition of the processes boundaries, and the variables and criteria that must be measured to quantify these indicators. Some indicators might be hard to quantify due to lack of data, however, it is essential to include such indicators qualitatively to ensure the multi-dimensionality of the assessment.

Boundary conditions

High-rate anaerobic reactors are used for anaerobic digestion in the wastewater treatment line. These respective technologies can also operate simultaneously on both lines of wastewater and sludge treatment, leading to the recovery of biogas from the wastewater sludge. All processes have the potential for bioeenrgy generation, hence, it is important to note the distinction between the different options when assessing the sustainability and defining indicators for the assessment. For instance, methodologies to evaluate the biogas potential are different from those of HTC and biomass steam gasification.

To simplify this distinction, two process boundaries must be identified, these are called the process-defined boundaries [60] and can be selected with the aim to compare between different processes and alternatives. It is important to note that a WWTP might employ bioenergy recovery in different forms such as biogas and hydrochar production. In this case, the assessment must require boundary extensions to include both lines (Figure 2).

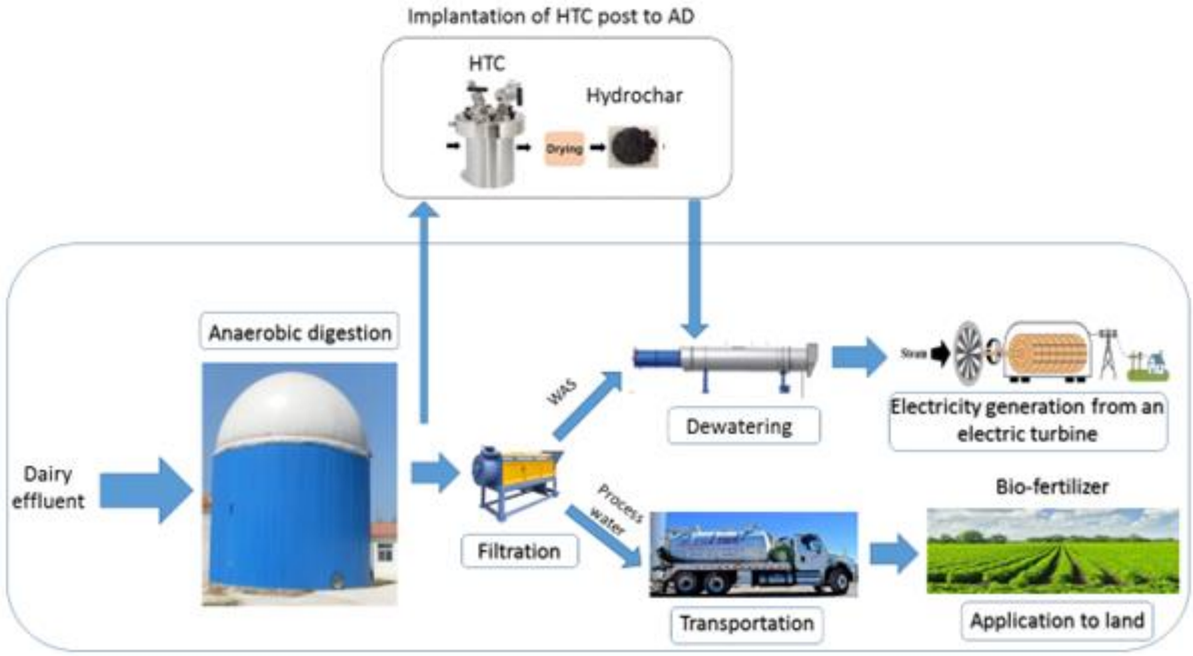

Figure 2. *HTC pretreatment system boundaries.*

The system boundaries for biogas recovery from a WWTP includes the high-rate anaerobic reactor, the influent into the reactor from the primary treatment, and the treated effluent from the reactor. The biogas produced from the reactor or the energy recovered in form of electricity and heat must be considered in the system boundaries. On the other hand, the system boundaries for bioenergy recovery from HTC includes the recovery of energy from the primary and waste-activated sludge. The end use of the digested and stabilized sludge must also be included in the process boundaries.

Indicators for the sustainability assessment framework

An LCA and a cost-benefit analyses can be beneficial to obtain a preliminary understanding of the potential amount of the bioenergy that can be recovered, including the energetics of HTC implementation. This preliminary data can also help gather approval from various stakeholders to further investigate the scope for the bioenergy recovery in their facility. To achieve this objective, a set of indicators along with the rationale for their selection must be discussed. Although there are several methods to utilize the biogas generated in a WWTP, the assumption here is about the energy recovery using co-generation of heat and power (CHP). CHP is the most widely used method to utilize the generated biogas, and it can be economically viable on a comparatively lower investment cost [28]. Based on previous recommendations, the indicators mentioned herein have been selected for their prevalence in existing academic research, and are representative of the crucial information that is the core of any feasibility study. They are transparent, easily quantifiable with well-defined methodologies, and are capable of clearly indicating the performance towards sustainability. Detailed descriptions of these methodologies about are presented in this section.

Technical indicators

a) Biogas Generation Potential: The estimated biogas generation potential from a substrate is the most important technical indicator. It is an essential indicator and it is used in research to indicate the quantity of biogas that can be generated per unit input, in terms of COD, BOD or volume of influent. The biogas generation potential can be calculated by several methods [10,61]. The theoretical methods are helpful in evaluating the potential for biogas recovery, thereby, precluding the need for extensive laboratory procedures and measurements. Even though this indicator is widely used, there is a lack of a standardized unit and methodology for reporting the biogas values, which makes it difficult to compare results from different studies to identify the best practices. The biogas generation potential from anaerobic treatment of a domestic WWTP can be estimated by the following Equation (3) [28].

$$Q_{BGAR} = Q_{SEW} * [S0(1-Y)-S] f(T) * CCH_4 * (1-IL) \qquad (3)$$

The description of the various factors is given in Table 4 [17].

__Table 4.__ Parameters for calculating biogas generation potential from wastewater.

Variable	Unit	Description	Assumption
Q_{SEW}	m^3/year	Total sewage flow into the anaerobic reactor	As per actual
S_0	kg/m^3	Influent chemical oxygen demand (COD) concentration to the reactor	As per actual
S	kg/m^3	Effluent chemical oxygen demand (COD) concentration	As per actual
Y	kg CODsludge/kg CODin	Solid production yield	0.17
f(T)		Volumetric correction factor due to temperature	
C_{CH_4}	%	Concentration of methane in biogas	60%
IL	%	Loss index of gas in the reactor due to leakage or dissolution	40%

The volumetric correction factor f(T) is calculated according to the following Equation (4).

$$f(T) = \frac{P \cdot K}{R \cdot T} \qquad (4)$$

Where P is the atmospheric pressure (1 atm); K is the COD consumed per production of 1 mol of CH_4 (64 g COD/mol); T is the average ambient temperature (298 K); and R is the universal gas constant (0.08206 atm.L/mol.K).

For biogas recovery from sludge, the methodology suggested by [60] is utilized based on the following Equation (5).

$$Q_{BGSS} = SS\frac{VS}{TS}E \cdot Q_{BGVS} \cdot P_{con}\frac{365}{1000} \qquad (5)$$

Variables are defined in Table 5 [17].

Table 5. *Parameters for calculating biogas potential from anaerobic sludge digesters [17].*

Variable	Unit	Description
Q_{BGSS}	m^3/year	Potential biogas generation from anaerobic digestion of sludge
SS	gSS/inh.day	Mass of sludge directed to the sludge treatment stage
VS:TS		Volatile-to-total solids ratio
E	%	Volatile solids removal efficiency
Q_{BGVS}	m^3/kg VS destroyed	Biogas production rate per kg of VS destroyed
P_{con}	inhabitants	Contributing population

b) Energy (Electricity and Heat) Generation Potential: The energy generation potential from biomass is important in evaluating the sustainability of the system. Electricity and heat generation using co-generation (CHP) is the most common and economically advantageous usage of the generated hydrochar [61]. Thus, it is important to quantify the potential electrical and heat energy that can be generated using a CHP system. Important parameters for evaluation include the CHP system efficiency and the calorific value of the produced biofuel. The quantification of electricity and heat generation potential can also help quantify the amount of fossil fuels that can be replaced with the generated energy, which can be another important parameter to evaluate the economic and environmental feasibility of the treatment process. The energy potential is usually reported in terms of kWh of energy per a functional unit (FU). The electricity generation potential from bioenergy recovery can be calculated using the following Equations (6) & (7).

$$P = LHV \cdot \eta \cdot Q_{BG} \cdot \frac{C_{CH4}}{31536} \tag{6}$$

$$E = P \cdot \Delta t \frac{f_c}{10^6} \tag{7}$$

The various factors in these equations are described in Table 6.

Table 6. *Parameters for calculating electrical energy generation potential.*

Variable	Unit	Description	Assumption
P	**KW**	**The electric power produced**	
LHV	MJ/m^3	Lower heating value of methane	35.5
η	%	Efficiency of the energy conversion technology	33
Q_{BG}	m^3/year	Biogas flow in Anaerobic Digesters	
C_{CH4}	%	Concentration of methane in biogas	60
		Factor for unit adjustment	31536
E	**GWh/yr**	**Annual Potential Electrical Energy**	
Δt	hours/yr	Annual hours of operation	8760
f_c		Annual capacity factor of the plant	0.8

The heat generation potential is the amount of the heat energy that can be recovered from the generated biofuel in a combined heat and power engine. Using the method applied by [25] in their analysis of biofuel potential, we can estimate the heat energy generation potential from the biofuel recovered in any WWTP. However, it is important to note that this is a preliminary estimation of the heat energy generation potential, and it will vary according to the process conditions, losses, and the recovery efficiencies of different technologies. The heat generation (GWh/yr) from biofuel produced in a WWTP can be described by the following Equation (8).

$$E_{th} = Q_{BG} \cdot LHV_{BG} \cdot \eta_{th} \frac{f_c}{10^6} \tag{8}$$

The various factors in the equation are described in Table 7.

Table 7. *Parameters for calculating thermal energy generation potential.*

Variable	Unit	Description	Assumption
E_{th}	GWh/yr	Amount of thermal energy from biogas	
Q_{BG}	m^3/year	Biogas flow in anaerobic digesters	As per actual
LHV_{BG}	kWh/m^3	Lower calorific value of biogas	5.5
η_{th}	%	Thermal efficiency of energy conversion technology	45
f_c		Annual capacity factor of the plant	0.8

c) Techno-economic analysis framework

A spreadsheet-based model can be developed based on literature to gauge all scenarios, specifically, those of the capital and operational expenditure impacts on the wastewater sludge management. In the past, treatment technologies was developed as an environmental management service, rather than focusing on biomass production as a profit-making activity [62]. Also, wastewater and sludge management projects have widely been identified as non-profitable even when revenues from the energy generation are considered. The estimation of the individual equipment purchase cost can be based on using cost correlations and capacity. All equipment’s must be constructed in stainless steel, to resist acids and corrosive materials such as H_2S. A material factor assumption is also necessary [62]. Fixed operation costs can be calculated as percentages from the revenues of the product sales. Main recommended assumptions are compiled in Table 8.

Table 8. *Parameters and assumptions for a techno-economic assessment.*

Parameter	Value/comment
Base year	2020 (September)
Currency	EUR
Plant lifespan	20 years
Plant location	Szeged (Hungary)
	Location Factor: 1.11[a]
Plant construction material	316 stainless steel
	Material factor (fm) = 1.3[b]
Equipment purchase cost (C_E)	Sum. of individual purchased equip.
Equipment erection	$C_{er} = C_E (f_{er}/f_m), f_{er} = 0.5$[c]
Piping	$C_p = C_E f_p, f_p = 0.6$[c]
Instrumentation and control	$C_i = C_E (f_i/f_m), f_i = 0.3$[c]
Electrical works	$C_{el} = C_E (f_{el}/f_m), f_{el} = 0.2$[c]
Civil works	$C_c = C_E (f_c/f_m), f_c = 0.3$[c]
Structures and buildings	$C_s = C_E (f_s/f_m), f_s = 0.2$[c]
Lagging and paint	$C_s = C_E (f_l/f_m), f_l = 0.1$[c]
Capital cost estimation ISBL	$ISBL = C_E + C_{er}+C_p+C_i+C_{el}+C_c+C_s+C_l$

OSBL	$OSBL = ISBL\ f_{OSBL},\ f_{OSBL} = 0.4$
Design and engineering (*D&E*)	$C_{D\&E} = ISBL\ f_{D\&E},\ f_{D\&E} = 0.25$
Contingency (X)	$C_X = ISBL\ f_X,\ f_X = 0.1$
Total investment cost (TIC)	$TIC = ISBL+OSBL+D\&E+X$
Operating cost	
Supervision	25% of OL
Direct salary overhead	60% of OL
Maintenance	5% of ISBL
Taxes and insurance	2% of ISBL
Rent of land and buildings	2% of (ISBL+OSBL)
General plant overhead	65% of OL+ supervision
Allocated environmental charges	1% of (ISBL+OSBL)
Fees	1% of TIC
Capital charges	1% of TIC
Variable production costs estimation	
Electricity	111€/MWh
Water	1.39€/t
Selling price of byproducts	
Hydrochar	104€/t

Electricity	57€/MWh

[a,b] *No specific factor was found for Hungary in the literature. We utilized the one reported for Germany in* [63].

d) Environmental Indicators (Life cycle assessment- LCA)

- Goal and scope: The goal of the LCA assessment is to evaluate the environmental performance of the treatment method. The system boundary starts when the dairy effluent reaches the WWTP and enter the AD digester which includes the biogas production and utilization, the water-solid separation, the transport and application of digestate to land (as a liquid fertilizer), and the transport and utilization of the dried deactivated sludge and hydrochar by combustion. Since the LCA analysis was not addressed in this work, this literature review is intended to set the basis to evaluate the environmental performance of the treatment methods. The attributional framework of HTC conditions was adapted based on previous findings. By-products production (energy from biogas and hydrochar, fertilizers in the form of digestate) will avoid the production of the corresponding market products and thus, reduce their environmental burdens.
- Life cycle inventory: The main parameters for LCI are summarized in Table 9, 10 and 11 and detailed in the following paragraphs.

Table 9. *Summary of the main parameters for the LCA inventory modeling.*

Parameter	Value	Unit
Anaerobic digestion		
Fugitive emission	4.00[a]	% of biogass
Digestate application to land		
Digestate transportation	100	km
N_2O emissions	3.00	% of N applied
NH_3 emissions	6.90	% of N applied
Nitrate emissions to groundwater	37.5	% of N applied
Nitrate emissions to surface water	14.0	% of N applied
P emissions to surface water	3.53	% of P applied
CH_4 emissions	0.05	% of C applied
C sequestered in soil	6.00	% of C applied
Plant-availability of N contained in the digestate	24.5	% of N applied
Plant- availability P contained in the digestate	73.0	% of P applied
Plant- availability K contained in the digestate	100	% of K applied
N_2O emissions following mineral fertilizers application	2.00	% of N applied
Nitrate emissions to groundwater following mineral fertilizers application	10.0	% of N applied
Nitrate emissions to surface water following mineral fertilizers application	4.00	% of N applied
Plant-availability of N contained in mineral fertilizer	67.0	% of N applied
Plant-availability of P contained in mineral fertilizer	73.0	% of P applied
Plant- availability K contained in the digestate	100	% of K applied
Hydrochar combustion		
Transportation	20	km
Heat conversion efficiency	70.0	% of LHV
CO_2 emissions	84.8	% of C applied
CO emissions	2.30	% of C applied
CH_4 emissions	0.60	% of C applied
NH_3 emissions	0.40	% of N applied
NO	1.20	% of N applied
SO_2	1.20	% of S applied
Steam gasification of hydrochar		
Transportation	20	km
CO_2 emissions	24.8	% of C applied
CO emissions	12.5	% of C applied
CH_4 emissions	2.50	% of C applied

Table 10. *Summary of the main parameters for the LCA inventory modeling during biofuel combustion.*

Parameter	Emission factor	Unit
Biogas combustion		
CO	310	g/GJ
NOx	202	g/GJ
Non methane volatile organic compounds	21.15	g/GJ
SO_2	25	g/GJ
Incineration of dry sludge		
CO	1.1	% of C applied
CO_2	60.9	% of C applied
CH_4 emissions	0.5	% of C applied
NH_3	0.6	% of N applied
NO	1.8	% of N applied
SO_2	1.1	% of S applied
Incineration of hydrochar		
CO	2.3	% of C applied
CO_2	84	% of C applied
CH_4 emissions	0.6	% of C applied
NH_3	0.4	% of N applied
NO	1.7	% of N applied
SO_2	1.4	% of S applied

Table 11. *Summary of the main parameters for the LCA inventory modeling during hydorchar production (HTC).*

Parameter	Value	Unit
Hydrochar production (HTC)		
CO_2	1	% of C applied
CH_4	0.4	% of C applied
H_2S	48	% of S applied

Fugitive emissions from the AD stage is 4.00% [62]. Emissions of C, N and P following the digestate application were modeled in previous study [62]. The application of digestate to land was assumed to avoid the production and application of N, P and K mineral fertilizers. The rate of the mineral fertilizers avoided is determined by the nutrient content in the digestate (N, P, and K) and the plant-availability of the digestate. The plant-availability of nutrients contained in the digestate was assumed to be 24.5% for N [36], 73% for P [64] and 100% for K [61]. On the other hand, the plant-availability for N contained in the avoided mineral fertilizers is 67% [64]. The metal content of the mineral fertilizers was calculated with average data obtained previously [62]. Since the application of metals to land can be relevant to human toxicity, a linear correlation must be considered between the toxicity potential and the amount of metals added. Same assumptions apply for HTC digestate. However, the overall mass balance shows slightly lower plant-availability for N (18.8%), P (42.8%) and K (89.9%). These observations were obtained previously [62] and could be attributed to the fact that more elements are retained in the produced hydrochar.

The produced hydrochar is easily transported and either combusted directly to produce electricity with heat conversion efficiency of 70% or is can be used in steam gasification to generate syngas. Because of the lack of the measured data associated with emissions for sludge hydrochar combustion, this inventory was adapted from [25]. H_2 combustion is assumed emission free. The impact associated with hydrochar disposal was created by [26]. Finally, the utilization of hydrochar must be assumed to avoid the environmental impact associated with the production, combustion and ash disposal of hard coal briquettes in a substitution ratio of 1 MJ: 1 MJ.

3. Objectives

The aim of this study is to characterize dairy sludge as a substrate for anaerobic digestion and examine the effectiveness of hydrothermal carbonization, microwave irradiation and ultrasound as a pretreatment and post treatment to enhance the digestion efficiency and its energy and nutrient recovery. The investigation was designed to achieve the following objectives:

a) Test the chemical composition and properties of waste sludge from different sites in Hungary for the determination of sludge suitability for AD.
b) Evaluate ultrasound disruption prior to MW disintegration on dairy sludge biogas production during AD.
c) Evaluate coupling anaerobic digestion with hydrothermal carbonization as a potential treatment to enhance the recovery of energy and nutrients.
d) Study the chemical transformations (the cycle of organic carbon and the dynamics of the functional groups) during each one of the tested treatment methods.
e) Evaluate the performance of hydrchar steam gasification compared to that of raw sludge.
f) Evaluate the mass and energy balance of implementing an HTC reactor in a functional WWTP.

Hydrothermal pretreatment is expected to enhance the efficiency of the anaerobic digestion by altering the dairy sludge chemical bonds and consequently facilitate the digestion of organics, which is expected to increase the portion of organics converted into methane. More so, MW irradiation is expected to enhance the biogas yield through the penetration of the water molecules to deposit the thermal energy and generate heat throughout the volume of sludge. This is expected to occur because of the higher intensity of hemicellulose degradation as a response to MW irradiation, which is not easily degraded by the anaerobes.

4. Materials and methods

4.1 Wastewater sampling and collection

Municipal wastewater samples were taken from the wastewater plant located in Kiskunhalas city (Hungary) while meat processing and dairy wastewater samples were collected from local factories in Szeged (10 L sample volume, each) for characterization. Dairy wastewater samples were used to create the dairy sludge and evaluate the pretreatment technologies as detailed herein. Two types of dairy sludge (82 wt.% and 96 wt.% water content, 10 L) were both provided from a local milk processing factory and were used as received in the experiments. A third type of waste was formed as a 50:50 mixtures (manual mixing using beaker and stirrer). All were preserved in a fridge at 4℃, and their moisture content was checked on a weekly basis. After sampling, sludge was dried at 105 °C for 24 h and stored in a desiccator prior to treatment.

Characteristics of dairy sludge prepared were as the following: pH (6.89), soluble COD (SCOD) was 0.8 g/L, total COD (TCOD) was 12 g/L, soluble biological oxygen demand (BOD_5) was 160 mg/L, total BOD_5 was 7 g/L. Total Solids (TS) content was 16.7 g/L. Volatile Solids (VSs) content was 9.6 g/L, and SS content was 7.5 g/L.

4.2 Ultrasound (US) disruption prior to MW disintegration

A lab scale concept design of ultrasound assisted microwave disintegration was studied in the first part of this work, and the operational conditions were evaluated for the dairy industry sludge treatment. The main objective of this part was to investigate the effect of sludge disruption via US prior to subsequent MW irradiation on sludge disintegration and energy recovery (Figure 3).

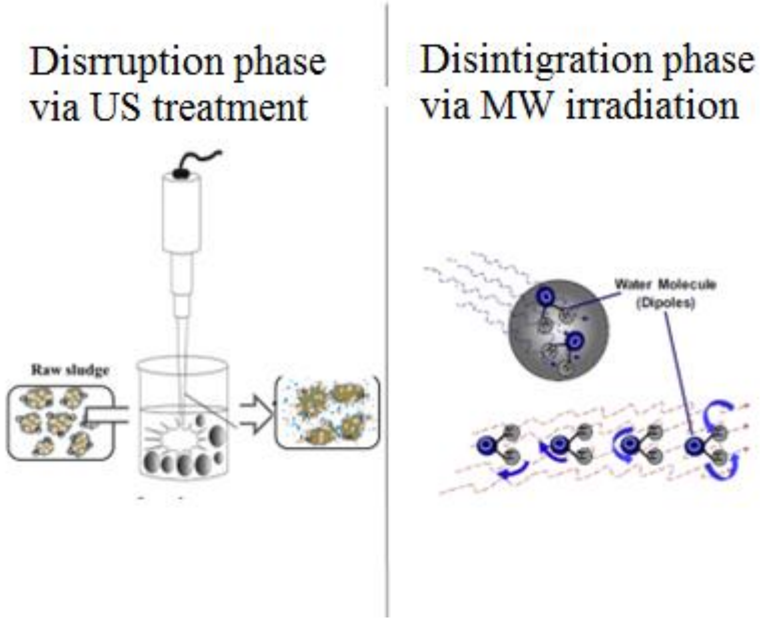

***Figure 3.** Ultrasound disruption prior to MW disintegration of dairy sludge.*

US pretreatment was carried out using Hielscher UP200S ultrasonic homogenizer (Germany) with operating frequency of 24 kHz, rated voltage (200-240 V), and rated current of 2 A. 500 mL of sludge were placed in a glass beaker without temperature adjustment (room temperature). US probe was submerged into the sludge to a depth of 2 cm. The effect of US pretreatment on sludge disintegration was evaluated at different processing times (10 s, 20 s, 30 s, 40 s, 50 s, 1 min, 2 min, 3 min).

According to [58] the rise in sludge temperature during US disruption at a short sonication time is not significant. However, sludge temperature was controlled during experimentation to avoid a vast increase during the treatment (Figure 4). Temperature of sludge was measured after US treatment and no significant increase was reported (<2°C). Each set of US conditions was performed in triplicates. Results were reported as mean values with standard errors.

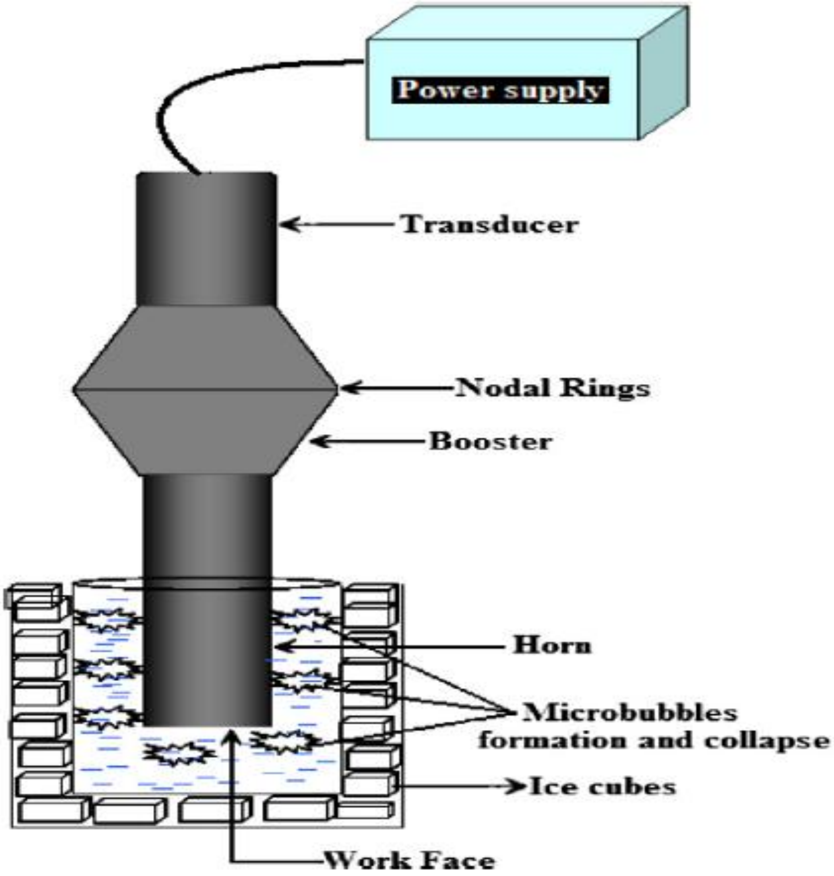

***Figure 4**. Ultra sonication of dairy sludge (temperature controlled)* [47].

4.3 MW disintegration

MW irradiation was performed by placing 250 mL of sludge in Bucher industrial microwave (78680-EPONE-FRANCE) oven with the following information:

Model: labotron. Type: 500. Date: 26.07.89. Series N: 1583. U: 120V. I: 10 A. Pn: 1.2 kVA. Ph: 1. I: 60 Hz.

MICRO-ONDES: Pa: 7.7 kVA. Pu: 0.5 kW. Umax: 4 kV. f: 2450 MHz.

AUXILIAIRES: Pa: 1.1 kVA.

Experiments were carried out in Polytetrafluoroethylene (PTFE) vessels for effective microwave dissipation in samples. A Cover was employed to avoid evaporation, volatile loss and hot spots formation during MW disintegration. Tests were performed at different treatment times, ranged from 0 to 6 min.

4.4 HTC reactor and experimental design

Samples of raw dairy sludge and digestate were first dried at 105 °C for 24 h and then mixed with double distilled water at 1:10 solid: water ratio and then introduced to 50 mL stainless steel tubular cylinder reactors. Each reactor consisted of a 27 mm diameter stainless steel pipe nipple and end cap. The reactors were heated by immersing them in a preheated Paratherm HR heat transfer fluid (Paratherm, Conshohocken, PA). One reactor was equipped with a temperature probe to provide a representative measurement of the temperature inside all reactors. Temperatures ranged between 180 and 240 °C with 30 °C intervals, and the reaction time was fixed at 30 min, not including the time needed to reach the desired reaction temperature. A schematic diagram of the HTC experimental setup is shown in Figure 5.

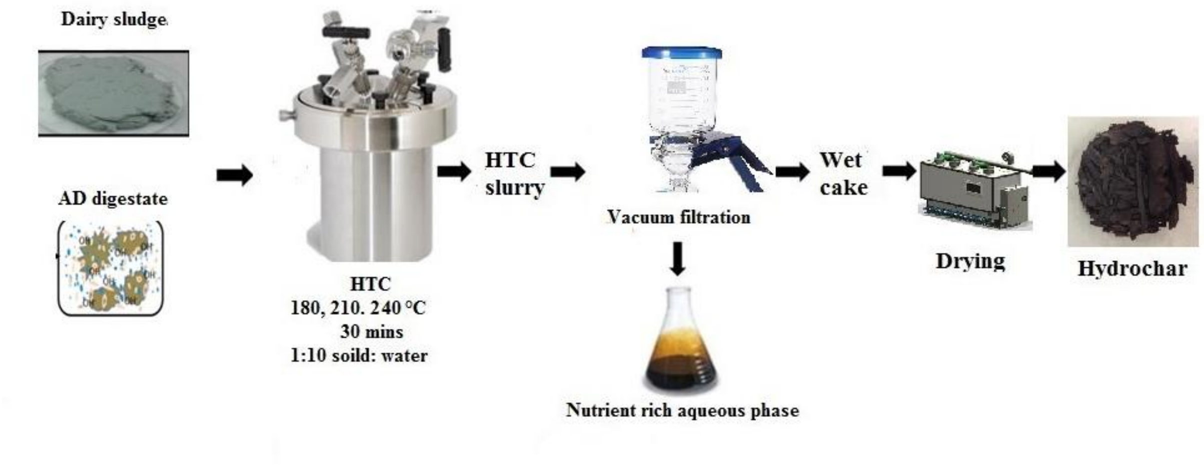

Figure 5. *HTC experimental set up.*

Following hydrothermal treatment, reactors were placed in ice bath to quench the reaction. Hydrochar was produced at 180°, 210° and 240 °C. All combinations of temperature were conducted in triplicates. The solid and aqueous phases were separated by vacuum filtration using 0.45 μm glass-fiber filter. Liquid products were collected in volumetric flasks whereas solid residues were allowed to dry overnight at 105 °C.

4.5 Hydrochar yield

The wet hydrochar was collected following filtration, weighed and then oven-dried at 105 °C for 24 h, and then weighed again to determine the hydrochar yield (recovered mass of the initial dry sludge). The effect of HTC temperature and residence time (combined) on the hydrochar yield was represented by HTC severity factor (f), Equation 9 [11].

$$f = 50t^{0.2}\boldsymbol{e}^{\boldsymbol{-3500/T}} \qquad (9)$$

where t is the reaction time (s), and T stands for the reaction temperature (K).

4.6 Aqueous phase analysis

pH and the electrical conductivity (EC) were measured using special electrodes and pH 150 meter (EUTECH INSTRUMENTS). TS and VS concentrations were determined according to procedures in standard methods APHA [65]. Dissolved organic carbon (DOC) and total nitrogen (TN) contents were determined by a Torch (Teledyne Tekmar, USA) combustion (HTC) type analyzer equipped with pressurized NDIR detector. Metals such as potassium, calcium, magnesium, sodium, iron and aluminum were analyzed using ICP analyzer (PerkinElmer 7000DV ICP-OES Spektrometer power of the radiofrequency-generator: 1450W) according to standard methods. Sodium absorption ratio (SAR) was calculated based on the concentrations of Na, Ca, and Mg. Samples were stored in a freezer prior to analyses (-18 °C).

4.7 Physicochemical properties

Samples were weighed and oven-dried at 105 °C for 24 h, and weighed again to determine TS and product yield (recovered mass). The organic matter was determined by combustion in a muffle furnace at 450 °C for 6 h. Elemental composition of C, H, N and S was determined with a FlashEATM1112 CHNS-O Analyser (Thermo Fisher Scientific Inc., UK). The O content was calculated as the remaining component after subtraction of C, H, N, S and ash. Higher heating value (HHV) was measured using bomb calorimeter (Thermo Fisher Scientific).

Molar element ratios, H/C and O/C were calculated using the measured element percentages and the known atomic weights of elements according to Equations (10) & (11). These data were used to calculate the energy yield and densification, and to plot the produced hydrochar on *Van Krevelen* diagram to evaluate its fuel quality based on previous literature [9].

$$Atomic\ H/C = \frac{Weight\ Percent\ Hydrogen/\text{Atomic Weight Hydrogen}}{Weight\ Percent\ Carbon/\text{Atomic Weight Carbon}} \tag{10}$$

$$Atomic\ O/C = \frac{Weight\ Percent\ Oxygen/\text{Atomic Weight Oxygen}}{Weight\ Percent\ Carbon/\text{Atomic Weight Carbon}} \tag{11}$$

4.8 FTIR Data processing

Dairy sludge and hydrochar were analyzed by Fourier transform infrared (FTIR) spectroscopy with a Nicolet 6700 Thermo equipped with a diamond smart ATR holder (Thermo Fisher Scientific Inc., UK) in the range of 4000–650 cm^{-1} through 36 scans. Spectra were corrected for background transmittance by subtracting the spectrum obtained with an empty holder. FTIR data processing was carried out after spectral acquisition using OPUS spectroscopy software (Bruker Optics). The analyzed absorbance spectral range was 3500 to 650 cm^{-1}. The statistical technique, PCA, was used to correlate spectral data and chemical behavior using SigmaPlot software. For the PCA, all FTIR spectra were vector-normalized to minimize noise and the effect of baseline shifts, and to highlight the changes due to the chemical composition.

4.9 Bio-Methane Potential (BMP)

BMP tests were conducted in 120 ml serum bottles. Inoculum of goat manure digestate was added from a biogas digester. Bottles were filled with 60 ml of substrate and then purged with nitrogen gas and sealed with rubber stoppers to ensure anaerobic conditions. Reactors were incubated at 37 °C. Gas pressure was measured and documented every 2-5 days using pressure meter (Lutron, PS-9302). Biogas production was determined following the ideal gas law, Equation (12).

$$pV=nRT \tag{12}$$

Where: p is pressure in Pascal, V is gas volume in m^3, R is gas constant (8.314 J /mol.K) ,and T is temperature in Kelvin.

Following gas collection, samples were stored at 10-mL glass vials sealed with a butyl valve and septum. Gas samples were analyzed for N_2O, CH_4 and CO_2 using CP-3800 gas chromatograph (Varian, Walnut Creek, CA) with a 0.53mm × 30mm Rt-Q-Bond column (Restec, Bellefonte, PA). CH_4 and CO_2 were analyzed with thermal conductivity detector using He as gas carrier (7mL/min) with sample volumes of 200 µl for CH_4 and CO_2 analysis. Temperatures of injector, column, and detector were 225 °C, 30 °C, and 225 °C, respectively. NH_3 and H_2S concentrations were estimated using a Kitagawa Gas Detector Tube System (Komyo Rikagaku Kogyo K. K., Japan) with a detection limit of 0.5 ppm and 100 ppm, respectively.

4.10 Theoretical BMP

The calculations of the theoretical BMP values were based on the elemental compositions of C, H, N and O using Boyle’s model, Equation (13).

$$BMP = \frac{22400\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}\right)}{12n+a+16b+14c} \tag{13}$$

where n, a, b and c represent the molar fraction of C, H, O and N, respectively.

4.11 Energy considerations

A detailed energy assessment was performed to evaluate the economic viability of each treatment technique. The equations employed to perform energy calculations are explained herein.

Input energy applied for US disruption and MW disintegration. Ultrasonic energy was applied to disrupt the flocs of sludge, whereas the microwave energy was consumed to disintegrate the sludge biomass during the pretreatment, both were calculated using the following Equation (14).

$$E = P \times T / (V \times TS) \tag{14}$$

where E is the input energy (kJ/kg TS), P is the input power (kW), T is the treatment time (sec), V is the volume of the sample (L) and TS is the total solids in the sample (kg/L).

The energy balance for each HTC reaction was obtained considering the wet feedstock as a nonreactive mixture of water and dry solids. Hence, the energy required to heat the sludge was calculated as the sum of the energy required to heat the water content and the dry feedstock separately based on Equation (15).

$$Q_{input} = m_w(H_{w;HTC} - H_{w;25}) + m_s C_P (T_{HTC} - 25) \tag{15}$$

Where Q_{input} is the energy input for the HTC process; m_w and m_s are the water and solids contents of the sludge, respectively. $H_{w,HTC}$ and $H_{w,25}$ are the enthalpy of water at the final HTC temperature and at 25 °C, respectively. C_p is the specific heat capacity of the dry feedstock, and T_{HTC} is temperature of HTC.

These amounts do not include the energy required for thickening and mixing inside the reactor, nor does it account for losses during biogas compression and purification. Still, with an optimized design and operational procedure, these amounts can be kept to a minimum.

The energy recovered in the form of methane was calculated based on the following Equation, (16).

$$R_m = T_m \cdot COD_s \cdot Y_m \cdot (-C_E) \cdot \alpha \qquad (16)$$

where, R_m is the methane energy recovery in kWh, T_m is total mass of sludge (kg), CODs is chemical oxygen demand in kg, Y_m is the yield of methane (m^3/kgCOD), C_E is the combustion energy of methane which is equivalent to 40 MJ/m^3 and α is the conversion factor for methane chemical energy to electricity, equivalent to 35%.

HTC output energy was calculated based on Equation (17).

$$Q_{output} = m_h \,.\, \Delta H°c \qquad (17)$$

where m_h is hydrochar mass and $\Delta H\ °c$ is hydrochar heat of combustion expressed as HHV.

4.12 Statistical analysis

The statistical analysis was performed to determine the differences between each parameter. First-way ANOVA was performed at 95% confidence level, when significant differences were detected, post hoc pairwise multiple comparisons were performed.

The Analysis of Variance (ANOVA) is a statistical method used to test whether there are significant differences between the means of two or more groups. ANOVA returns two parameters:

F-test score: ANOVA assumes the means of all groups are the same, calculates how much the actual means deviate from the assumption, and reports it as the F-test score. A larger score means there is a larger difference between the means.

P-value: P-value tells how statistically significant the measured values are.

ANOVA to return a sizeable F-test score and a small p-value.

By convention, when the

- p-value is < 0.001: There is strong evidence that the difference is significant.
- the p-value is < 0.05: There is moderate evidence that the difference is significant.
- the p-value is < 0.1: There is weak evidence that the difference is significant.
- the p-value is > 0.1: There is no evidence that the difference is significant.

5. Results and discussion

5.1 Wastewater characterization

Wastewater characteristics were measured to determine the initial properties and potential digestibility (Table 12). The organic fraction (volatile solids) ranged between 53% -60% with no significant difference (P>0.05). The total dissolved solids' (TDS) values were between 788 mg/L and 715 mg/L for both meat processing and municipal wastewater, respectively. However, low values of TDS were reported in dairy wastewater (150 mg/l). This might be attributed to the high rates of fats in dairy wastewater which limit the transport of the soluble substrates, which in turn, cause the conversion rate to decrease [4].

Table 12. *Wastewater characterization form three different sites. Standard error is shown in parentheses. Statistical differences are indicated by different superscript letters.*

Parameter	Dairy wastewater	Meat processing wastewater	Municipal wastewater
TS (g/l)	4.0^a	2.5^a	3.0^a
	(0.3)	(0.4)	(1.1)
VS (%) of TS	60^a	53^a	54^a
	(1)	(7)	(4)
TDS(mg/l)	153^a	788^b	715^b
	(2)	(72)	(81)
pH	5.35^a	6.05^b	7.08^c
	(0.10)	(0.01)	(0.01)
EC(mS/cm)	2.15^a	1.25^b	1.26^b
	(0.25)	(0.01)	(0.19)

The salinity of wastewater estimated by its EC was relatively low (<2.5), and the pH values were in the acceptable range (5-7). However, the potential use of the aqueous phase as a liquid fertilizer does not depend only on the salinity of the irrigation water, but also on the Sodium Absorption Ratio (SAR). The SAR is a measurement of the suitability of water for the use in agriculture, and is determined by the concentrations of Na^+ relative to those of Ca^{+2} and Mg^{+2}. Sodicity, high sodium concentrations, can cause swelling and dispersion of the soil clays, surface crusting and pore plugging, leading to a reduced infiltration and increased runoff [66]. However, the presence of the divalent ions, namely Ca^{+2} and Mg^{+2} can mitigate this impact.

All processing wastewaters exceeded the allowable discharge level of COD (300 mg/L), and BOD_5 (50 mg/L) (Table 14). However, the meat processing wastewater had significantly higher concentrations of BOD_5 than those of dairy wastewater ($P<0.05$). On the other hand, the concentrations of BOD_5 for municipal wastewater were slightly higher than expected [21]. This could be attributed to the fact that wastewater with high concentrations of BOD_5 is being discharged and mixed with the domestic wastewater in the sewage system before reaching the WWTP facility. The relatively high COD values in dairy wastewater is a result of the elevated concentrations of fats in dairy wastewater. However, the relatively low COD/BOD ratio (<10) suggests a degradable effluent with high organics suitable for anaerobic digestion. In general, the COD, BOD, pH, TS, and other major elements were all beyond the allowable discharge limits. Therefore, further treatment is needed and required.

Table 13. *COD and* BOD_5 *values of different types of wastewater (Hungary). Standard error is shown in parentheses. Statistical differences are indicated by different superscript letters.*

Parameter	BOD_5 (g/L)	COD (g/L)	COD/BOD_5 ratio
Municipal wastewater	1.9^{a}	2.0^{a}	1.1
	(0.2)	(0.2)	
Dairy wastewater	2.2^{a}	3.5^{a}	1.6
	(0.0)	(0.8)	
Meat processing wastewater	3.0^{b}	2.9^{a}	1.0
	(0.0)	(0.4)	

5.2 Ultrasound disruption prior to microwave disintegration

5.2.1 Determination of the specific energy input for US disruption

EPS release is expected to enhance biomass disintegration potential and increase the biodegradation rate during AD [67]. A sequential increment in EPS release was achieved via US up to 1,500 kJ/kg TS input energy, the increase after that was more intense indicating the end of the disruption phase (Figure 6). US processing generated a momentum in the growth of the microscopic bubbles, a phenomenon referred to as the cavitation effect. This phenomenon led to the formation of the hydroxyl radicals responsible for attacking the sludge floc matrix and disrupt it [19]. As a result, EPS matrix transformed into the soluble form, resulting in higher concentrations of proteins and EPS in the aqueous phase. In other words, the sonication forces caused a decrease in the firmness of the suspended solids (SS), which led to the lysis of the cells and the release of intracellular components into the aqueous phase [29].

The initial concentrations of the dissolved EPS in dairy sludge were under the detection limit (>50 mg/L) and increased to about 111 mg/L at the end of the disruption phase. A relatively higher trend of EPS release was observed after that (an increase from 111 mg/L to 200 mg/L as a response to only 500 kJ/kg TS increase in the input energy) implying the beginning of the disintegration phase. We can examine sludge phase change from floc disruption to cell lysis by measuring the differences in DNA concentrations. In previous research, DNA concentrations showed a mild increase during US disruption proving that the extraction of the exogenous EPS in the absence of cell lysis is possible at low US input energy [30]. Similar to EPS, the concentrations of the soluble proteins increased during US pretreatment. These results are similar to those obtained previously [29] for municipal sludge with lower input energy, probably due to the differences in energy considerations and sludge characteristics.

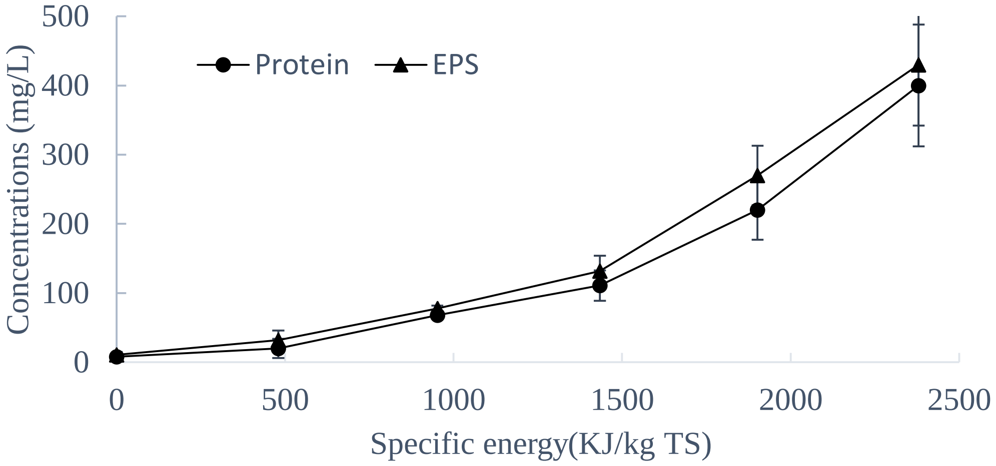

Figure 6. *The effect of ultrasound disruption with different energy input on floc disruption of dairy sludge. Error bars represent the standard errors.*

5.2.2 US disruption effect on SCOD release and SS reduction

In addition to protein and EPS release, the soluble chemical oxygen demand (SCOD) is another important indicator to evaluate the efficiency of sludge solubilization. US disruption improved the bioavailability of the particulate materials by increasing the rate of SCOD release as evident in Figure 7. SCOD release increased rapidly with the increase in the specific energy up to 600 kJ/kg TS. These results are in similar trend to those obtained previously in a semi-continuous anaerobic digestion reactor [68]. The rapid increase in SCOD release is attributed to the higher vulnerability of sludge for US effect in the disruption phase. Hence, the decrease in SCOD release at the end of the disruption phase is due to the diminution of the easily disintegrable organics. Another indication of the pretreatment efficiency on sludge stability is the suspended solids (SS) reduction. A rapid decrease in SS concentrations was observed during the first stage of US pretreatment (Figure 7). The main reason of the mass reduction in sludge during US disruption is the intense release of the extracellular and intracellular matters [68]. A slower trend in SS reduction was observed beyond the disruption phase attributed to the higher compression forces because of the higher intensity of the gas bubbles formation [69]. Similar conclusions were observed previously for waste activated sludge at a higher pH range [70].

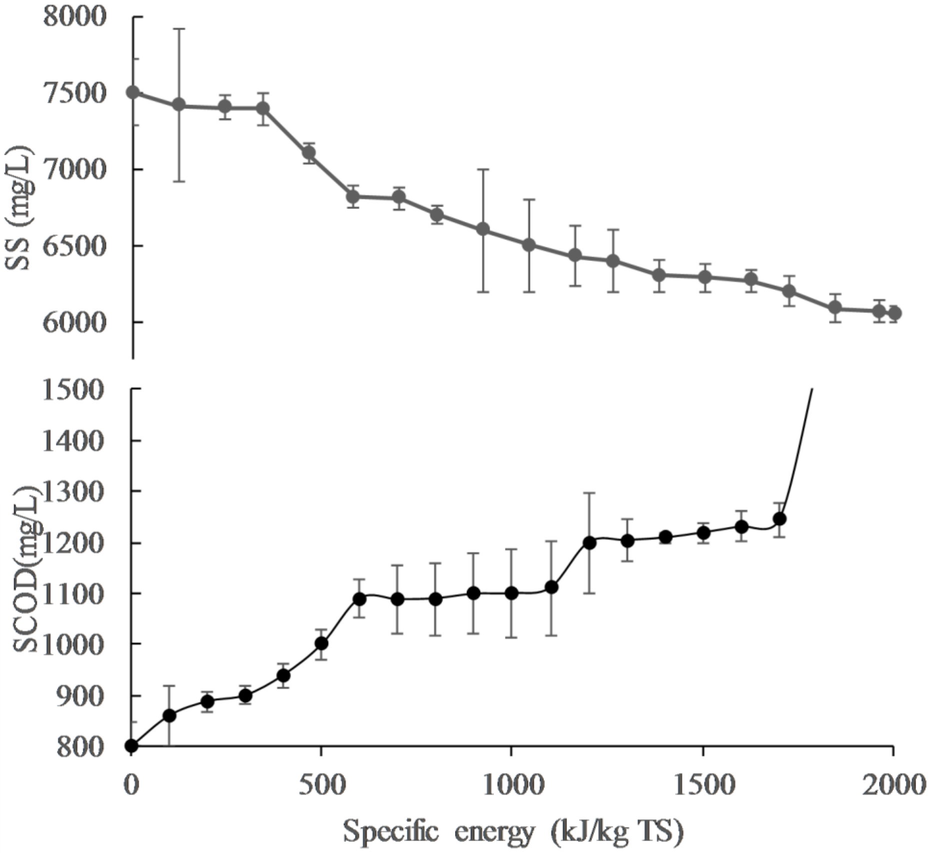

Figure 7. *The Effect of ultrasound disruption on COD solubilization and SS reduction of dairy sludge. Error bars represent the standard errors.*

5.2.3 The Effect of MW irradiation on sludge temperature

Sludge temperature is an essential parameter due to its effect on the sludge physical and chemical characteristics during MW disintegration [46]. Figure 8 shows the effect of MW irradiation on sludge temperature during the pretreatment process. Evaporation occurred gradually during the pretreatment process resulting in the carbonization of the humic substances of the organic matters [71]. The rapid heating of these particles during the pretreatment process was resultant by the molecular rotation; mainly because of the high frequency of the electromagnetic radiation that is interacting with the dipolar molecules of the organic matters [72]. However, high temperatures means higher energy consumption, which is uneconomical for sludge application [3].

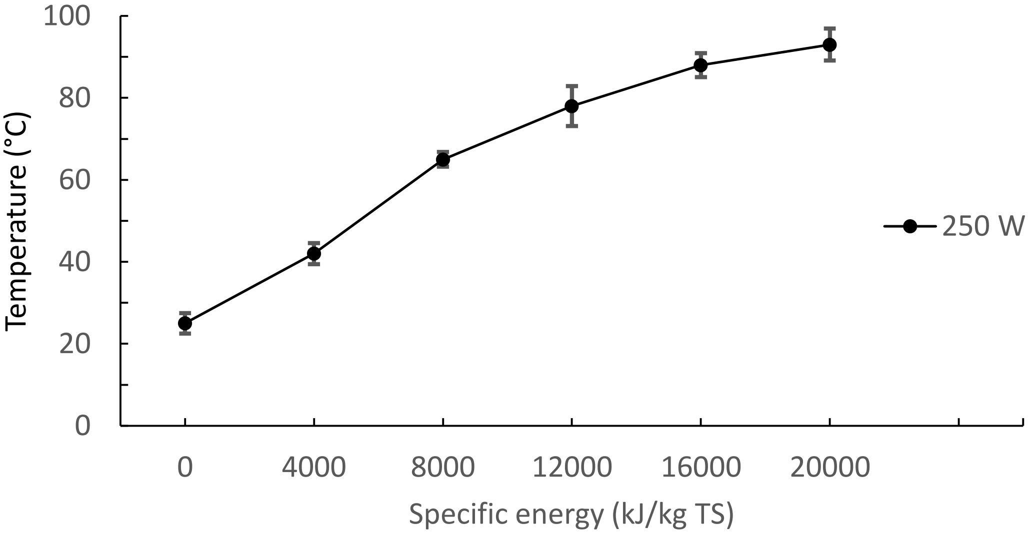

__Figure 8.__ The effect of microwave irradiation specific energy on dairy sludge temperature.

Only a handful of studies evaluated the effect of MW disintegration on sludge temperature during AD batch reactor performance, and they give conflicting results. For example, [73] evaluated MW irradiation at 100 °C and their results showed a significant increase in sludge dewaterability after MW irradiation. On the other hand, [74] claimed that increasing sludge temperature under MW irradiation from 72 to 93 °C did not improve the sludge disintegration significantly, and hence, MW disintegration at low temperatures were the most cost-effective in terms of COD solubilization per unit of energy. In this study, the optimal MW disintegration conditions were determined according to the amounts of SCOD that were released to the aqueous phase, a phenomena described in the next section.

5.2.4 Determination of the optimal specific energy input for MW disintegration

MW irradiation is expected to enhance the COD solubilization and SCOD release by breaking down the complex floc structures and increase the biodegradability of the organics. Figure 9 shows the effect of MW irradiation on COD solubilization and SCOD release in dairy sludge. US disruption (deflocculated sludge) resulted in higher trend of SCOD release. Initial SCOD concentrations of deflocculated sludge were on average 1,090 mg/L and increased to their maximum value at 1,780 mg/L at specific input energy of 12,000 kJ/kg TS, no increase in SCOD release was observed after that. Lower trends in SCOD release was obtained for flocculated sludge, starting at 800 mg/L, with a maximum value of 1,389 mg/L at the same specific input energy of 12,000 kJ/kg TS. The intense increase in SCOD release during MW disintegration was due to the intense hydrolysis of the large organic molecules caused by MW irradiation. These findings are consistent with those obtained previously [75,76], in which higher levels of hydrolysis were achieved after MW disintegration at low temperatures ($T < 96$ °C). In this experiment, sludge solubilization increased from 0.07 ± 0.01 to 0.12 ± 0.01 in flocculated sludge, and from 0.09 ± 0.01 to 0.15 ± 0.01 in deflocculated sludge subsequent to MW disintegration (Figure 9). The noticeable decrease in SCOD release beyond 93 °C (20,000 kJ/kg TS) was attributed to the higher intensity of the chemical reactions, including dehydration and decarboxylation. The optimum solubility of sludge was 15%, lower than that reported previously for municipal sewage sludge (22%) due to the higher presence of non-soluble organics in dairy sludge.

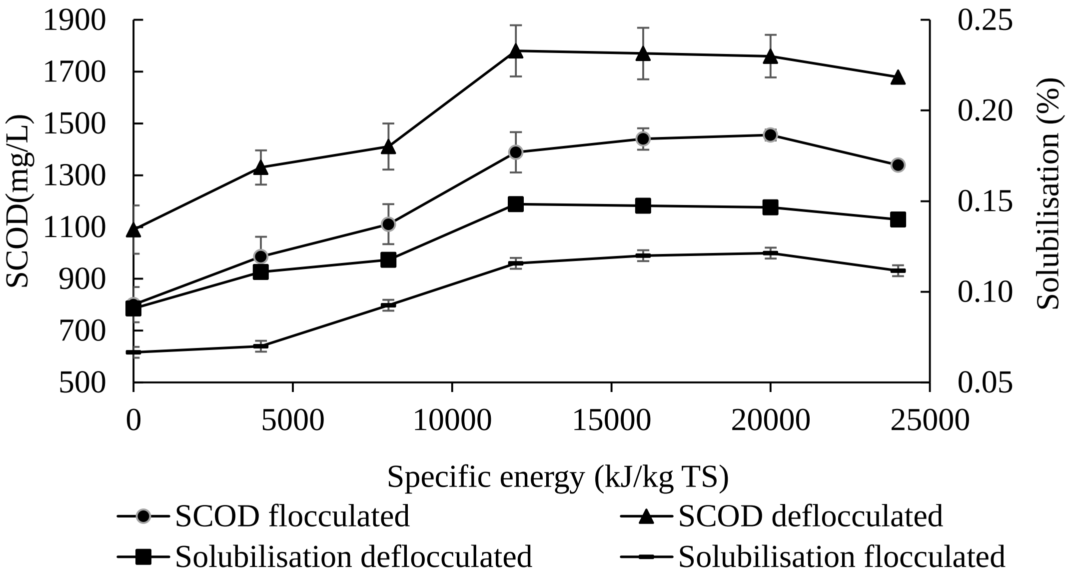

***Figure 9**. The Effect of microwave disintegration on COD solubilization and SCOD release in dairy sludge. Error bars represent the standard errors.*

5.2.5 SS reduction during microwave disintegration

SS reduction increased progressively for both deflocculated and flocculated sludge over the course of the MW pretreatment (Figure 10). The mass content decreased by 7.4% and 8.3% in deflocculated and flocculated sludge, respectively. The high rate of SS reduction during MW disintegration in sludge was due to the liquefaction of the readily biodegradable matters [30]. However, lower SS values in deflocculated sludge suggests its better adeptness to MW disintegration. The existence of unstable flocs in flocculated sludge reduced its disintegration potential through MW irradiation whereas flocs disruption via US prior to MW irradiation resulted in higher SS reduction. No significant increase in SS reduction was obtained beyond the specific energy input of 16,000 kJ/kg TS. These outcomes are similar to those obtained previously for waste activated sludge via disperser induced microwave disintegration [30]. P-value for SS concentrations (Table 14) were less than 0.01 revealing a significant variation between deflocculated and flocculated sludge.

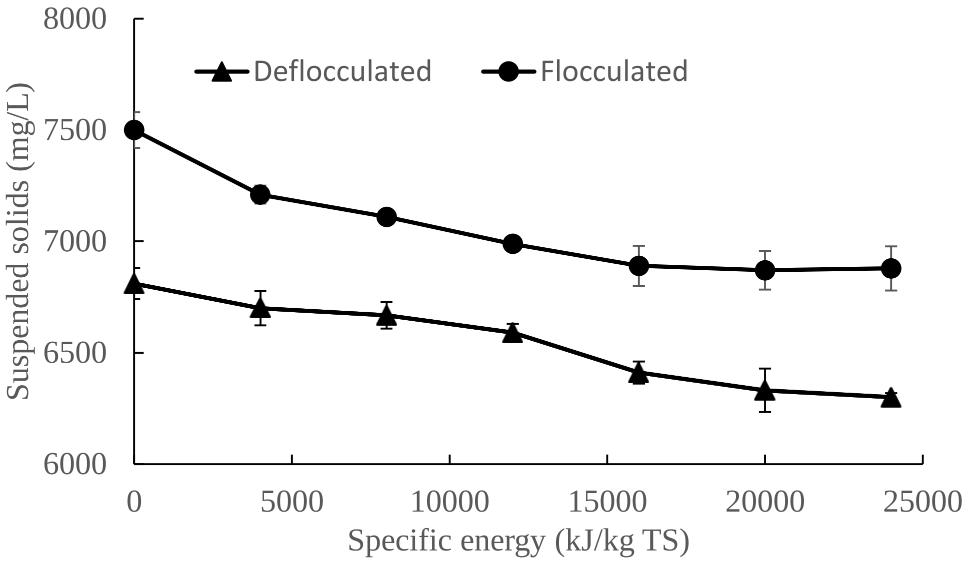

Figure 10. *The Effect of MW disintegration on the SS reduction in dairy sludge. Error bars represent the standard errors.*

Table 14. *Single way ANOVA of SS reduction during MW disintegration.*

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1292704	1	1292704	178.5092	0.000181	7.708647
Within Groups	28966.67	4	7241.667			
Total	1321671	5				

5.2.6 Fermentation study

Proteins and carbohydrates are the main organics in sludge composition. In the hydrolysis phase, proteins are converted into peptides and amino acids, and then to organic acids, NH_3 and CO_2. Whereas carbohydrates are transformed into polysaccharides [30]. The quantity of proteins in dairy sludge exhibited an increment during MW disintegration from 50 mg/L to 200 mg/L and 400 mg/L, in flocculated and deflocculated sludge, respectively. The carbohydrates concentrations increased from 5 mg/L to 24 mg/L and 59 mg/L, in flocculated and deflocculated sludge, respectively. Higher solubility of polymers such as proteins and carbohydrates causes higher rates of VFAs generation [77]. The importance of VFAs comes from its representation of a major class of organics in sludge intermediate products during the course of AD. Hence, the production and consumption balance of VFAs is vital for an efficient AD process. High

VFAs accumulation can cause low methane production and, subsequently, less energy gain [57]. The effect of MW disintegration on VFAs generation is presented in Table 15. The relative increase of butyric acid was the most significant (784%), followed by iso-butyric acid (213%) and acetic acid (167%). Similar observations were obtained previously in a semi-continuous anaerobic digestion reactor [6].

Table 15. *The effect of MW disintegration on VFAs concentrations in flocculated sludge. Statistical differences are indicated by different superscript letters.*

Parameter (mg/L)	Raw sludge (flocculated)	Disintegrated sludge (sole MW treatment).	Relative increase (%)
Acetic acid	371± 30^a	999± 49^b	167
Propionic acid	53± 10^a	133±77^b	151
Butyric acid	61±21^a	539±72^b	784
Iso-Butyric acid	319±19^a	992±119^b	213
Caproic acid	140±25^a	340± 87^b	143
Total VFAs	944	3003	218

5.2.7 Solid–aqueous phase characteristics

The concentrations of all parameters studied were, on average, higher in treated slurry, indicating higher solubility into the aqueous phase after the pretreatment process (Table 16). C concentrations increased significantly after MW disintegration, as the caloric value of sludge, suggesting that no (significant) losses in total C during MW irradiation occurred. Contrary to C, N concentrations decreased significantly in response to raising temperatures and spontaneously changed the C/N ratio. High total ammonia–nitrogen (TAN) concentrations in the aqueous phase indicates high TAN release. TAN accounted for about 33–37% of TN present in the aqueous phase after the pretreatment process, with undetectable concentrations of NO_2 and NO_3. The rest of N fraction are believed to be aliphatic and aromatic nitrogenous compounds [50].

Table 16. *The effect of MW disintegration on the aqueous-solid phase characterization for dairy sludge. Statistical differences are indicated by different superscript letters.*

Parameter (mg/L)	Raw sludge (Flocculated)	Disintegrated sludge (Sole MW treatment).	Relative increase (%)
C	59 ± 0^{a}	65.4 ± 2.3^{b}	67.1 ± 0.3^{b}
N	4.5 ± 0.2^{a}	5.1 ± 0.5^{a}	3.7 ± 0^{b}
C/N	9.3	9.8	15.9
TS	37 ± 7.8^{a}	30.6 ± 6.8^{b}	30.8 ± 1.8^{b}
HHV	23 ± 1^{a}	29 ± 0^{b}	29 ± 0^{b}
Aqueous phase			
pH	6.85^{a}	5.38^{b}	5.29^{b}
EC (ms/cm)	3	4	3.3
DOC(mg/L)	822 ± 101^{a}	4993 ± 205^{b}	5523 ± 74^{b}
Macronutrients			
TN (mg/L)	$140^{a}\pm70$	$229^{b}\pm70$	$266^{b}\pm10$
TAN (mg/L)	$50^{a}\pm7$	$76^{b}\pm3$	$90^{c}\pm0$
P (mg/L)	36^{a}	156^{b}	116^{b}
K	195^{a}	624^{b}	672^{b}

Secondary nutrients			
Ca	$290^{a}\pm6$	$439^{b}\pm11$	$607^{c}\pm19$
Mg	$284^{a}\pm6$	$522^{b}\pm2$	$414^{b}\pm10$
S	98^{a}	150^{b}	130^{b}
Micronutrients			
Cu	32^{a}	85^{a}	76^{a}
Na	859^{a}	668^{a}	654^{a}
Zn	13	20	30
SAR^{c}	8.6^{a}	5.1^{b}	5.0^{b}

^{a,b} Statistical differences are indicated by different superscript letters.

^{c}Na +/(0.5 * (Ca^{2+} +Mg^{2+}))$^{0.5}$ where all concentrations are in meq/L.

N and P recovery is essential during wastewater treatment since they are scarce and non-renewable [78]. High concentrations of macronutrients in the aqueous phase were reported, such as N, P and K. On the other hand, the concentrations of micronutrients such as Mg and Ca, were as low as 280–300 mg/L, while S concentrations were less than 100 mg/L. Other micronutrients such as Zn and Cu were detected at even lower concentrations, 13 mg/L and 32 mg/L, respectively. In general, the concentrations of Mg, Ca, Cu and K increased after MW disintegration due to the hot water leaching. These results are consistent with those obtained previously for other hydrothermal treatment techniques [56,79].

SAR is another measurement to determine the effect of AD slurry on soil clays when used in irrigation, and it can be calculated by measuring the concentrations of Na relative to those of Ca and Mg. The aqueous phase of dairy sludge had a moderately high SAR (Table 16). However, higher recovery of Mg and Ca after MW disintegration resulted in a slightly lower SAR. Another indication of the effect of MW disintegration in sludge solubility is the dissolved organic carbon (DOC). It is noticeable that DOC concentrations increased significantly from 822 mg/L to 4,993 mg/L and 5,523 mg/L, in flocculated and deflocculated sludge, respectively.

This increase is attributed to the reduction in the particles' sizes during US processing, as well as due to the raise of sludge temperature during MW disintegration [37].

The decrease in pH after MW pretreatment is corresponded to the high production of VFAs which was the main reason of low methane production during the first stage of AD [34,57,80]. However, the currently observed values are more acidic than those previously reported for dairy sludge [81]. The high acidity obtained in the present study is most likely due to the higher intensity of VFAs production and accumulation in the AD batch reactor.

5.2.8 Biodegradability assessment

The results of the BMP assay are presented in Figure 11. The relatively low biogas production at the first stage of the BMP assay (0–10 d) was due to the high generation of VFAs due to the intense hydrolysis. Clearly, methane production was trivial in the first 10 days as a consequence of poor methanogenesis [57]. Subsequent to 10 days, the production of biogas experienced a significant enhancement in deflocculated samples. Over the period of 60 days, an average increase of 50 mL/gVS was observed in sole MW disintegrated samples (flocculated sludge). The increase was almost 90 mL/gVS (compared to control) with US disruption (deflocculated sludge). Methane concentrations in all samples remained constant at approximately 60–65%.

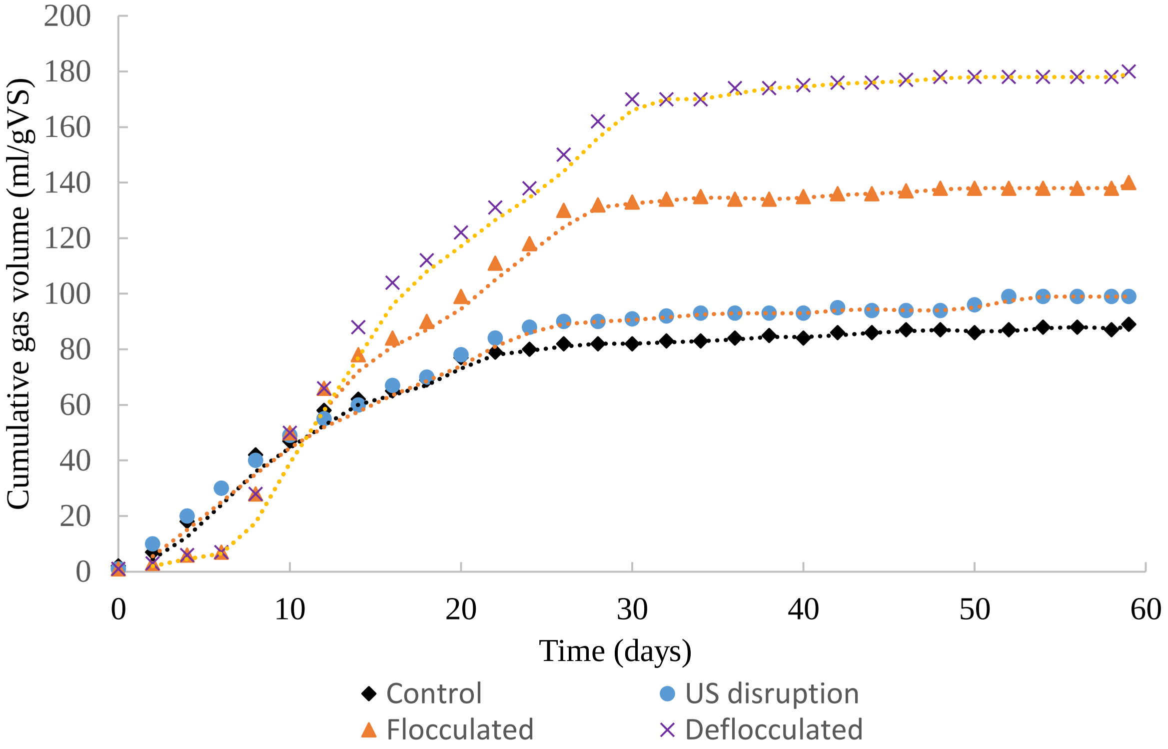

Figure 11. *Plot showing cumulative biogas production of different pretreatments (dairy sludge).*

Low methane generation in sole US treated samples is attributed to the lack of easily accessible substrates due to insufficient pretreatment. Methane generation in MW disintegrated samples was higher due to the higher availability of the released organics. However, flocculated sludge generated less methane than that of the deflocculated sludge, which could be related to the slower hydrolysis rate. Higher methane production in deflocculated sludge is a clear indicator that US disruption increased the availability of the organic substrates within the biomass, which led to an enhanced conversion rate of the organics during methanogenesis [3]. These outcomes were similar to those obtained previously via disperser induced microwave disintegration [29] except for the first 10 days. Unfortunately, the latter mentioned study did not report the pH values nor the VFAs concentrations during AD. The amount of methane produced in this study was expressed in terms of ml/gVS. The mass balance calculations revealed higher VS removal corresponded with the higher methane production rate implying that higher fractions of VS were converted to methane.

5.2.9 Energy assessment

Energy equilibrium results are presented in Table 17. To calculate the total energy consumption, the energy employed for US and MW pretreatment were taken into account. However, the energy needed for stirring and heating the reactors during AD were not included as they are depended mainly on the operation design. A 15% optimum solubilization was set as an index to investigate the energy consumption. Total energy employed per kg of sludge to attain the 15% solubilization was 5.55 kWh and 3.75 kWh in flocculated and deflocculated sludge, respectively. Hence, nearly 70% of the input energy was consumed to attain the desired solubilization. The input energy of the combined process was lower than that obtained previously [82]. This could be connected to the long pretreatment times required to attain the desired solubilization in dairy sludge. A positive net energy of about 26 kWh per kg sludge was obtained in the combined treatment, which is higher than what obtained previously [29]. The difference in our results was due to the differences in the energy considerations and sludge initial characterization. Based on the obtained results, it can be confirmed that sludge disruption via US prior to MW disintegration is believed to be a cost effective and feasible process.

Table 17. *US and MW energy balance assessment.*

Parameter (per kg of sludge)	Deflocculated	Flocculated	Unit
Energy content of methane	30	23.5	kWh
Energy applied	3.75	5.55	kWh
Net energy production	26.25	17.95	kWh

5.3 Coupling hydrothermal carbonization with anaerobic digestion

5.3.1 The effect of HTC conditions (severity factor) on hydrochar yield

The HTC processing temperature is an essential parameter because of its effect on the physicochemical characteristics of the produced hydrochar. Typically, carbonization occurs when the reaction mechanism shifts from ionic to free radical under saturation conditions [83]. During HTC reactions, the increase in temperature causes a decrease in water viscosity, creating easier penetration into the porous media and subsequent degradation of the organics [2]. In contrast, a pyrolysis-like process is likely to occur if the HTC processing temperature was insufficient to break up the major components [84]. Table 18 lists the data showing the effect of HTC processing temperature and residence time on the hydrochar yield. The hydrochar yield decreased significantly with increasing temperature because of the intense decomposition of the large molecules into smaller components (aqueous phase) and incondensable low molecular gaseous products [85]. Hence, a higher fraction of the aqueous phase is expected to form at higher HTC temperatures, resulting in higher solubility and elemental extraction [10].

***Table 18**. Comparison of the effects of temperature and residence time (severity factor) on hydrochar yield formation as reported by the previous studies and the present investigation.*

Biomass	Temperature (°C)	Residence time (min)	Severity factor (*f*)	Water content (%)	Hydrochar yield (%)	Reference
Poultry litter	180	60	0.11	67	74.8	[9]
	200	60	0.16	67	60.7	
	220	60	0.21	67	58.1	
	250	60	0.32	67	46.1	
Human excreta	180	120	0.13	75	69.2	[11]

	210	120	0.21	75	64.9	
	230	120	0.32	75	55.6	
Dairy sludge	225	120	0.12	82	55	[20]
	225	120	0.12	89	61	
	225	120	0.12	96	70	
	250	120	0.16	82	58	
	250	120	0.16	89	76	
	250	120	0.16	96	79	
	250	240	0.19	82	70	
	250	240	0.19	89	77	
	250	240	0.19	96	83	
Dairy manure	200	240	0.09	95	58.3	[85]
	220	240	0.12	95	51.6	
	240	240	0.16	95	49.6	
	260	240	0.21	95	44.4	
	280	240	0.27	95	43.5	
DS digestate	180	30	0.10	91	50.3	This work
	210	30	0.16	91	30.2	
	240	30	0.21	91	27.0	

DS	180	30	0.10	91	80.4	This work
	210	30	0.16	91	68.4	
	240	30	0.21	91	69.3	

Nonetheless, HTC gaseous products (CO_2 >80%, with small fractions of CH_4, H_2S and NH_3) were formed intensely at high temperatures, as demonstrated in Figure 12. At the same time, there was a notable decrease in CO_2 concentrations with increasing temperatures, accompanied by a slight increase in CH_4 and H_2S concentrations (data not shown). Similar observations were also reported previously for different types of feedstock [10,86]. Generally, high HTC processing temperatures lead to the intense decomposition of the solid residue, which is expected to reduce the hydrochar yield [87].

Another important parameter that affects hydrochar yield formation is the HTC residence time. A long residence time is expected to enhance the severity of HTC reaction. Previous studies reported that HTC residence time had a similar but smaller effect on the hydrochar yield formation [20]. Therefore, HTC residence time can play an important role in determining the degrees of dehydration and decarboxylation during the process. Hence, controlling the HTC residence time was essential in the current work to produce hydrochar with desired characteristics and to minimize the energy consumption. The effect of HTC severity factor on hydrochar yield is represented in Figure 12.

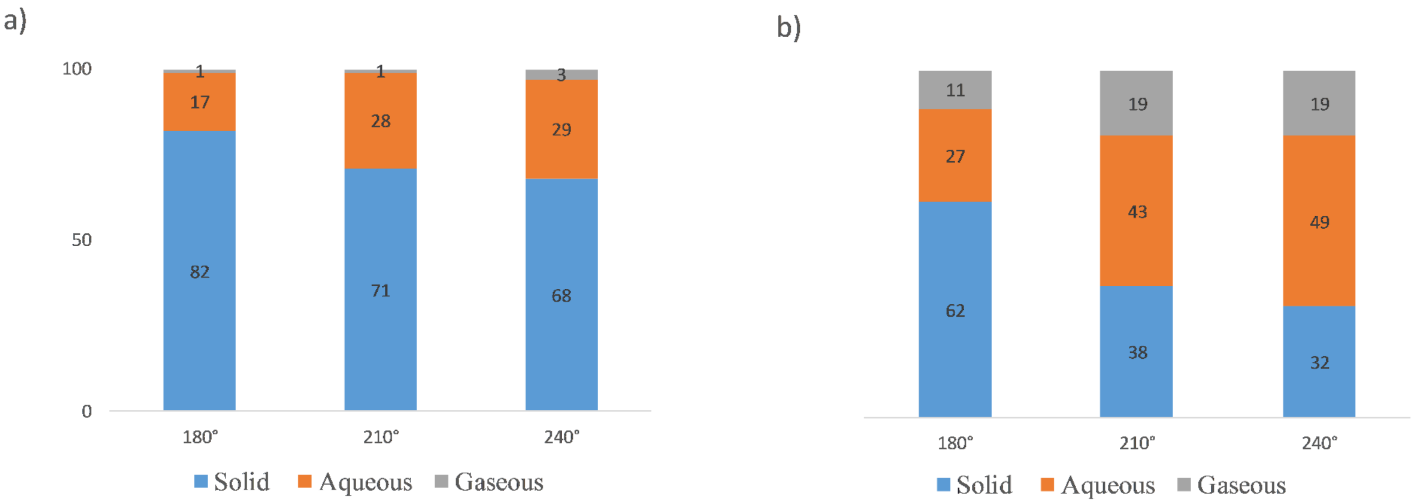

Figure 12. *HTC pdroduct yeild formation a) raw dairy sludge, b) AD digestate (°Celsius).*

The (f) values obtained from previous studies were calculated in this work to ensure a comprehensive comparison (Table 18). Generally, higher hydrothermal severity generates lower hydrochar yield except for the results obtained by [20]. This phenomenon could be due to the high ash content in the feedstock [88]. Another reason for a higher hydrochar yield is the intense polymerization of the soluble oxygenated fragments such as furfural and 5-hydroxymethylfurfural in severe HTC conditions, resulting in the formation of the secondary char, increasing the overall hydrochar yield [89].

5.3.2 Solid-phase characteristics

Physicochemical properties

The results of the proximate and ultimate analyses of all (dried) samples are listed in Table 19. Proportions of the organic matter in dairy sludge were, on average, higher than those in the digestate. However, the N content in the digestate did not vary (P-value> 0.05), suggesting that most of N remained in the solid phase after the AD. Presumably, N is bound to the cell wall proteins and interwoven with the structural carbohydrates and lignin [90]. In contrast, C content decreased significantly after AD. Anaerobes use C for cell growth and energy production, whereas N is consumed to synthesize amino acids, proteins, and nucleic acids. Theoretically, anaerobes consume C 30 times faster than N during AD. Similar to C, lower levels of H were detected in the digestate. However, the relative increase in C content after the HTC processing of the dairy sludge digestate was higher than that obtained from raw dairy sludge, indicating higher carbon recovery. Similarly, HHV values increased significantly (P-value <0.05) in both substrates after HTC. However, not all of the energy released during HTC is stored in the produced hydrochar. Hence, hydrochar energy yield was calculated for both substrates to quantify the percentage of the energy recovered in the final product. The energy yield in the produced hydrochar ranged between 89-93% and 35-57% for raw dairy sludge and dairy sludge digestate, respectively. Higher energy recovery in raw dairy sludge-derived hydrochar could be attributed to lower mass losses during HTC. Lower mass losses in raw dairy sludge could be ascribed to the lower ash content and higher organic matter content than those in dairy sludge digestate (Table 19). The atomic ratios H/C and O/C for raw dairy sludge and dairy sludge digestate shifted from the upper right to the lower left in the *Van Krevelen* diagram as HTC proceeded (Figure 13). This movement indicates higher intensities of dehydration than decarboxylation during HTC. This finding is consistent with that observed previously at different solid to water ratio [20]. As seen in Figure 13, AD digestate evolved progressively from compositions falling within the range of biomass, peat, and lignite to a material that is closer in composition to coal. Whereas raw dairy sludge shifted to the range of lignite as HTC advanced, indicating lower fuel quality. In summary, AD digestate hydrochars generated at 210 and 240 °C had H/C and O/C ratios of 0.6 – 1.0 and 0.15 – 0.2, respectively. These ratios for raw dairy sludge hydrochars were 0.8 - 1.2 and 0.22 – 0.27, respectively.

***Table 19**. Proximate and ultimate analyses of dairy sludge and digestate. Standard errors are shown in parentheses.*

Parameter	Dairy sludge	Digestate	Sludge-char			Digestate-char		
			180°	210°	240°	180°	210°	240°
Proximate analyses								
Ash (%)	28^a	61.2^b	29.2^a	29.1^a	30.3^a	61.1^b	61.8^b	62.0^b
	(3.2)	(6.1)	(1.8)	(2.5)	(3.3)	(1.6)	(2.0)	(1.4)
Volatile solids (VS)	72^a	38.8^b	70.8^a	70.9^a	69.7^a	38.9^b	38.2^b	38.0^b
(%)	(8)	(0)	(7)	(1)	(9)	(8)	(11)	(3)
Ultimate analyses								
C (%)	37.5^a	18.8^b	44.2^c	54.0^d	56.4^d	29.9^e	31.1^e	31.6^e
	(2.2)	(2.9)	(0.9)	(4.1)	(1.3)	(2.0)	(3.5)	(1.1)
H (%)	4.8^a	2.2^b	5.1^a	5.3^a	5.3^a	2.6^b	2.7^b	2.4^b
	(0.0)	(0.1)	(0.1)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
N (%)	1.7^a	1.5^a	2.1^b	2.4^b	2.4^b	4.1^c	3.5^e	3.5^e
	(0.1)	(0.1)	(0.1)	(0.0)	(0.0)	(0.0)	(0.1)	(0.0)
S (%)	0.5^a	0.1^a	0.5^a	0.5^a	0.4^a	0.1^a	0.1^a	0.1^a
	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
O (%)	27.9^a	14.3^b	23.5^c	21.8^c	21.1^c	12.6^d	8.2^e	6.5^e
	(1.6)	(2.0)	(1.5)	(1.2)	(0.9)	(0.6)	(1.0)	(0.4)
HHV_{ex} (MJ/kg)	15.1^a	7.8^b	17.2^c	18.5^c	19.4^c	9.1^d	10.2^d	10.0^d
	(1.3)	(0.6)	(0.9)	(0.9)	(1.1)	(0.2)	(1.9)	(1.1)
HHV_{th} (MJ/kg)	18.2	8.8	20.7	23.9	24.6	12.8	13.2	13.0
Energy yield[1]			93%	89%	89%	57%	37%	35%
Energy densification[2]			1.4	1.2	1.3	1.2	1.3	1.3

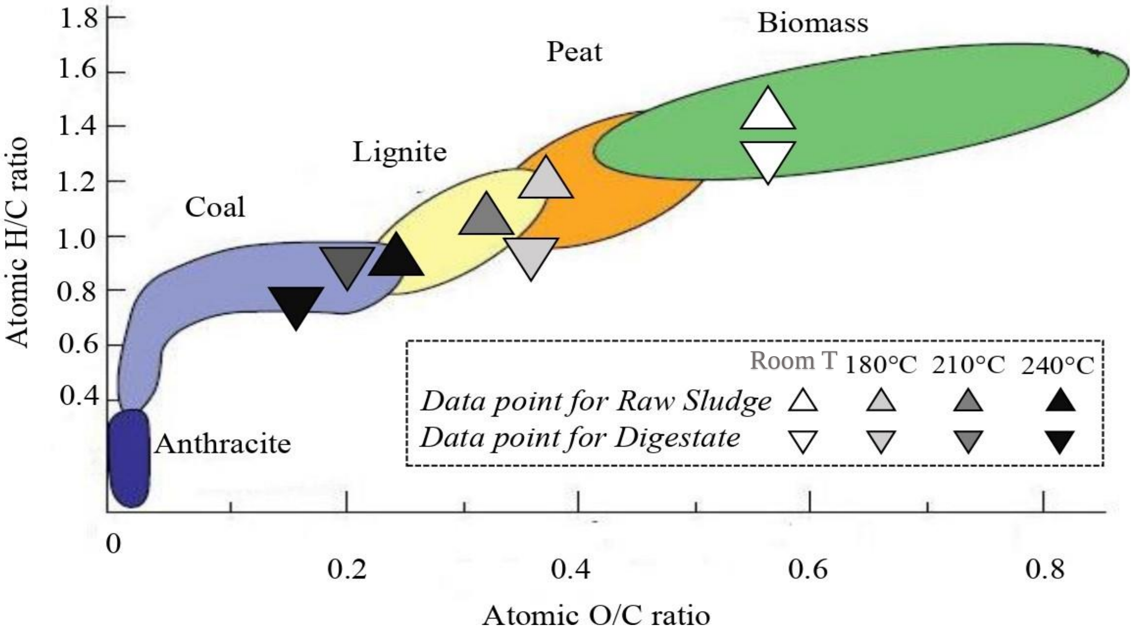

Figure 13. *Van Krevelen diagram of hydrochar produced from raw (dairy) sludge and AD digestate with solid:water ratio of 1:10. Standard errors ranging from 0.001 to 0.04 for atomic H/C ratio and 0.07 to 0.093 for atomic O/C ratio..*

FTIR analysis

An FTIR spectroscopic analysis was performed to better understand the difference in the chemical compositions during HTC processing. The FTIR spectra at 210 °C showed peaks are identified herein [10, 55, 70, 97, 98].

The peaks observed below 1000 cm^{-1} were attributed to aromatic –CH out-of-plane bending vibrations indicating a continuous conversion of the aromatic structures during HTC.

Other peaks were typical to –COH band (at 1051 cm^{-1}). The relative increase in the intensity of these peaks during HTC is associated with a shrinking –COH bond in alcohols.

The peak at 1378 cm^{-1} is linked to C-H vibrations of alkyl and methyl groups. A relatively high intensity of this peak was observed after HTC processing indicating that, as other components in the feedstock are degraded during HTC, methyl becomes more present.

The peaks between 1500 and 1700 cm^{-1} are linked to carboxylic acid derivatives, namely amides and amino acids. The relative increase in the intensity of this peak in the digestate is attributed to the amide band, specifically Amide-I, out-of-stretching vibrations in the carbonyl group.

The peaks at 2850 and 2970 cm^{-1} are attributed to aliphatic C—H stretching and aromatic C—H bending vibrations, respectively.

The peaks between 3,200 and 3,400 cm^{-1} are probably derived from the (–OH) band in hydroxyl and carboxyl groups, indicating the existence of free and intermolecular bonded groups. The relative increase in the spectrum intensity at 3250 cm^{-1} is due to the intense dehydration at high HTC temperatures [85].

5.3.3 Aqueous -phase characteristics

HTC aqueous phase characteristics are summarized in Table 20. Concentrations of all parameters considered in the digestate were, on average, higher than those obtained in raw dairy sludge except at 240 °C indicating higher elemental extraction. The relative decrease in concentrations at 240 °C is due to the significant losses in mass at high HTC processing temperatures [9]. Initially, the aqueous phase of raw dairy sludge had a pH of 9.34, which decreased to 7.4 - 7.8 after HTC. In contrast, dairy sludge digestate pH decreased from 7.44 to 5.4 - 5.6 after the treatment process. The decrease in pH corresponds to the formation of organic acids and CO_2 during the carbonization of the cellulosic feedstock [9]. The higher acidity in dairy sludge digestate occurred due to the higher degradation of sugars into short-chain carboxylic acids such as formic acid, acetic acid, propionic acid, and lactic acid. Identifying these compounds in the aqueous phase (Table 21) evokes the dehydration mechanism demonstrated in Figure 13. These results are consistent with those obtained previously for the sewage digestate [93].

Table 20. *Aqueous-phase characterization of dairy sludge and digestate after HTC treatment (Standard errors are shown in parentheses).*

Parameter	Sludge				Digestate			
	Raw	180°	210°	240°	Raw	180°	210°	240°
Total solids (TS)	452.5^a	153.0^b	226.3^a	235.8^a	222.2^a	122.4^b	104.0^b	106.0^b
	(6.7)	(1.3)	(4.3)	(8.5)	(7.7)	(2.2)	(10.0)	(6.0)
pH	9.3^a	7.4^b	7.8^b	7.7^b	7.44^c	5.4^d	5.4^d	5.6^d
	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
EC (mS/cm)	6^a	8^a	16^b	14^b	16^b	18^b	26^c	24^c
	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
DOC (mg/L)	822^a	1991^b	2303^b	1765^b	1987^b	3791^c	4102^c	3222^c
	(101)	(78)	(201)	(49)	(21)	(39)	(102)	(56)
Macronutrients								
TN (mg/L)	140^a	292^b	291^b	303^b	229^b	316^b	618^c	620^c

	(61)	(18)	(25)	(33)	(06)	(24)	(20)	(14)
TAN (mg/L)	36^{a}	73^{b}	73^{b}	76^{b}	68^{b}	79^{b}	155^{c}	154^{c}
	(5)	(6)	(5)	(0)	(2)	(0)	(1)	(1)
P (mg/L)	36.1^{a}	70.8^{b}	70.9^{b}	59.7^{b}	164.3^{c}	221.4^{c}	138.2^{c}	138.0^{c}
	(1.0)	(8.7)	(11.1)	(9.9)	(14.4)	(13.2)	(21.1)	(12.3)
K (mg/L)	252.9^{a}	299.1^{a}	268.9^{a}	250.8^{a}	309.5^{b}	322.2^{b}	312.1^{b}	298.1^{b}
	(100)	(296)	(201)	(198)	(95)	(149)	(301)	(89)
Secondary nutrients								
Ca (mg/L)	43.0^{a}	44.2^{a}	54.0^{b}	56.4^{b}	139^{c}	144^{c}	111^{c}	116^{c}
	(2.9)	(0.9)	(4.1)	(1.3)	(11)	(21)	(35)	(11)
Mg (mg/L)	50^{a}	151^{b}	153^{b}	153^{b}	199^{b}	226^{b}	270^{b}	249^{b}
	(1.0)	(1.0)	(0.0)	(0.0)	(2.0)	(0.0)	(0.0)	(0.0)
S (mg/L)	21.5^{a}	21.0^{b}	24.0^{b}	24.0^{b}	52.0^{b}	41.0^{b}	35.0^{b}	35.0^{b}
	(2.0)	(1.0)	(0.0)	(0.0)	(1.0)	(0.0)	(1.0)	(0.0)
Micronutrients								

B (mg/L)	1.0^a	0.5^a	0.5^a	0.4^a	1.0^a	0.1^a	0.1^a	0.1^a
	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
Cl (mg/L)	143^a	235^a	218^a	211^a	266^a	226^a	282^a	265^a
	(20.0)	(15.0)	(12.0)	(19.0)	(81.0)	(16.0)	(10.0)	(14.0)
Cu (mg/L)	32^a	17^a	18^a	19^a	85^a	19^a	10^a	10^a
	(6)	(1)	(1)	(1)	(5)	(2)	(1.9)	(1.1)
Fe (mg/L)	21^a	15^a	13^a	12^a	30^a	18^a	18^a	19^a
	(0)	(1)	(1)	(2)	(8)	(11)	(1)	(6)
Na (mg/L)	293^a	357^a	337^a	335^a	406^b	493^b	489^b	389^c
	(35)	(17)	(11)	(16)	(11)	(13)	(41)	(29)
Zn (mg/L)	2.0^a	1.4^a	1.2^a	1.3^a	1.0^a	1.2^a	1.3^a	1.3^a
	(0.1)	(0.1)	(0.0)	(0.0)	(0.0)	(0.3)	(0.0)	(0.2)
SAR	7.2^a	5.7^a	5.9^a	5.3^a	5.2^a	5.8^a	5.7^a	4.5^a

Table 21. *VFAs concentrations in dairy sludge.*

Parameter (mg/L)	Raw dairy sludge	HTC aqueous phase	Relative increase (%)
Acetic acid	331± 71^a	949± 99^b	187
Propionic acid	51± 13^a	173±37^b	240
Butyric acid	62±11^a	579±52^b	834
Iso-Butyric acid	319±19^a	912±199^b	186
Caproic acid	120±45^a	380± 47^b	216
Total VFAs	883	2993	239

DOC concentrations increased after HTC (180° and 210°) to 765- 2,303 mg/L in raw dairy sludge and 3222- 4102 mg/L in dairy sludge digestate, respectively. In contrast, DOC concentrations tended to decrease at 240 °C owing to the significant losses in TC during HTC processing at high temperatures. Similar to TC, TN concentrations increased after HTC processing (Table 20). Similar observations were obtained for total ammonia nitrogen (TAN). TAN accounted for about 33-38% of TN with negligible concentrations of NO_2 and NO_3. Moreover, higher concentrations of macro, micro, and secondary nutrients were reported after HTC processing at 180 and 210 °C, suggesting the use of HTC's aqueous phase as a liquid fertilizer. The concentrations of most elements in the aqueous phase decreased at 240 °C owing to the higher absorption ratio in the porous structures at high processing temperatures [51].

The concentration of P increased from 36.1 to 59.7 - 70.8 mg/L in raw dairy sludge after HTC. However, no significant increase was reported in P and K concentrations in dairy sludge digestate after carbonization (P-value > 0.05). A fertilizer must also be a source of secondary and micronutrients such as Cl, Mg, S, and Na. The concentrations of Cl ranged between 143 and 282 mg/L, whereas Mg and S concentrations were 50- 270 and 21.5- 52 mg/L, respectively. Moreover, the micronutrient Fe was detected at concentrations of 12- 30 mg/L. Low concentrations (1–2 mg/L) of Zn and B were also detected.

Raw dairy sludge aqueous phase salinity, represented by EC, increased from 6 mS/cm before HTC to 16 mS/cm after the process. A more distinct increase in EC was observed for dairy sludge digestate (26 mS/cm). The aqueous phase had a moderately high SAR. Hence, further investigation is required to determine the means to improve the characteristics of the aqueous phase and confirm that all nutrients are bioavailable. In addition, the advanced characterization of the aqueous phase intermediates and their degradation products is essential to detect any toxicity or microbial inhibition.

The composition and utilization of the HTC gaseous products were problematic in the current work owing to analytical limitations. There is, therefore, a gap in the present study regarding the potential use of HTC gaseous products.

5.3.4 Biogas production

BMP experimental results are shown in Figure 14. Methane production appeared to cease after 30 days. HTC processing at 180 °C did not improve the contributions of VFAs concentrations in the batch reactors. On the other hand, VFAs concentrations at 240 °C did not contribute to the methane yield potential owing to the inhibitory effects caused by the toxic compounds generated at high HTC temperatures. However, VFAs concentrations at 210 °C contributed substantially to the methane yield potential. This assumption was supported by the significant increase in COD solubilization, indicating higher degrees of sludge biodegradability after HTC pretreatment. These results are consistent with those obtained previously for waste-activated sludge [84,94].

Low methane generation in raw sludge samples is attributed to the lack of easily accessible substrates. In contrast, methane production after HTC pretreatment increased because of the higher availability of the organics. However, hydrochar generated at 180 °C produced less methane than that produced at 210 °C because of the insufficient pretreatment. Higher methane production after HTC is a clear indicator of the increased availability of the organic substrates within the biomass, which leads to an enhanced conversion of the organics during methanogenesis (methane production). The amount of methane produced is expressed in terms of ml/gCOD (Figure 14). The theoretical methane potential results are listed in Table 22. BMP_{th} was slightly higher than BMP_{exp} except at 240 °C. Higher theoretical values were expected as Boyle's equation does not account for the non-biodegradable organics. Moreover, not all of the biodegradable organics present in the feedstock are consumed by the anaerobes [32].

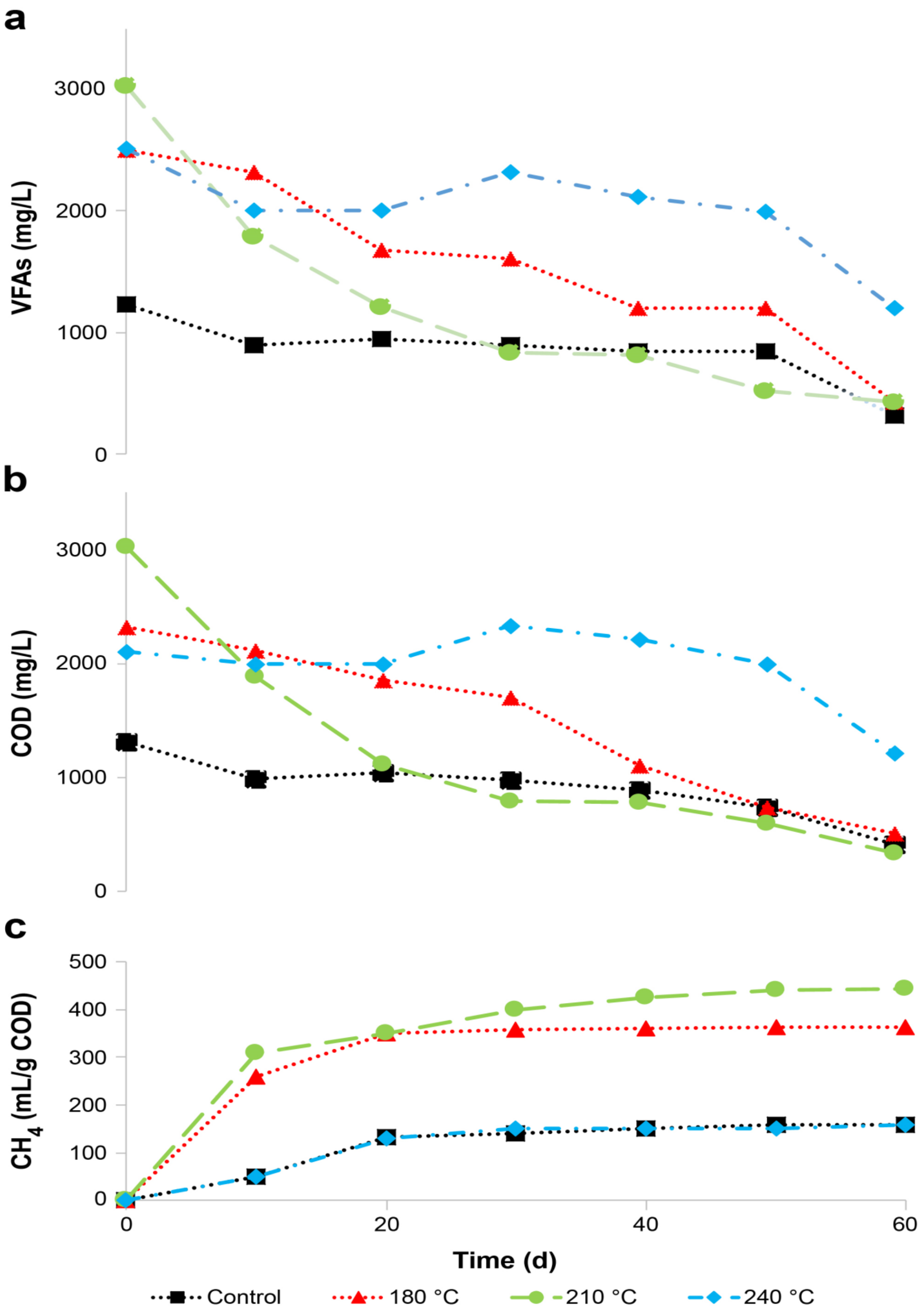

Figure 14. *Variations in (a) VFAs, (b) COD, and (c) cumulative CH_4 production during the BMP assay of dairy sludge.*

Table 22. *Comparisons of the experimental BMP and theoretical BMP (Boyle's Equation).*

Sample	BMPexp (mL CH_4/g COD)	BMPth Boyle's Equation (mL CH_4/g COD)	Biodegradability, Boyle's Equation (%)
Control	152 ± 30^a	258 ± 49^b	59
180°	363 ± 10^a	378 ± 77^b	96
210°	444 ± 21^a	500 ± 72^b	89
240°	158 ± 9^a	546 ± 119^b	29

5.3.5. Energy balance and hydrochar utilization

To investigate whether the HTC of raw dairy sludge and digestate offers advantages when combined with AD, different valorizing approaches were evaluated. The energy balance for all approaches evaluated in the current work is summarized in Table 23. The energy employed for HTC processing in these calculations was considered at 210 °C. Energy inputs for all HTC processing temperatures investigated in this work are shown in Table 24. As demonstrated in Table 23, the total energy production obtained by HTC post-treatment increased when the produced hydrochar was utilized in H_2 production by steam gasification.

Table 23*. Energy balance of all valorization approaches considered in this study.*

Per kg of sludge	AD (no treatment)	HTC pretreatment to AD	HTC posttreatment to AD (Incineration)	HTC posttreatment to AD (hydrochar steam gasification)	Unit
Energy content of methane	1.5	4.48	1.5	1.5	kW h
Energy applied for HTC processing	--	0.2	0.2	0.2	kW h
Energy content of hydrochar	--	--	2.53	--	kW h
Energy input for steam gasification	--	--	--	0.73	kW h
Energy content of syngas	--	--	--	4.63	kW h
Net energy production	1.5	4.28	3.83	5.2	kW h

Table 24. *HTC energy balance.*

Temperature	Energy input (kJ/kg of sludge)		
	Energy to heat water	Energy to heat dry content	Total energy to heat sludge
180°	599	20	619
210°	714	23	737
240°	857	27	884

Steam gasification of raw dairy sludge hydrochar was performed at 900 °C, and steam to biomass (S/B) ratio of 1.5. A high S/B ratio shifts the reaction equilibrium towards H_2 formation and promotes steam reforming of hydrocarbons. However, an S/B ratio higher than 1.5 decreased H_2 concentration in the produced syngas (data not shown). This observation could be explained by the short residence time of the thermal and hydrocracking reactions with the increase in the steam flow rate [95]. Similarly, H_2 content decreased gradually with increased temperatures exceeding 900 °C. This decrease is attributed to the fact that the reverse reaction during steam gasification is faster than the forward reaction at temperatures above 900 °C. A similar tendency was observed during steam gasification of municipal solid waste [96].

The H_2 content of hydrochar was significantly higher than that of dairy sludge digestate at the same temperature and for the same S/B ratio. Gas yield from steam gasification of dairy sludge digestate was about 1.02 Nm^3/kg compared to 1.543 Nm^3/kg for hydrochar. HTC-derived hydrochar is rich in hydrophilic functional groups. Therefore, it is dispersed easily in the water molecules during steam gasification [97]. Thus, a higher amount of unbound H atoms is generated during hydrochar steam gasification compared to raw digestate. Additionally, higher concentrations of inorganic matter and metals are expected to increase the evolution of gas composition during steam gasification. In other words, the increased metal content within the produced hydrochar resulted in higher gasification reactivity and conversion efficiency.

5.4 Case Study Using Developed Sustainability Assessment Framework – Szeged, Hungary

A comparison between two technological scenarios for dairy sludge management were evaluated in this section. Both scenarios were contemplated to achieve (or approach) energy self-sufficiency. Therefore, heat integration and internal consumption of electricity were taken into account. The description of these scenarios is given herein.

- Standalone AD scenario: This scenario consisting in biogas production to generate electricity through a steam engine.
- HTC and AD integration: This combined method consisting the treatment of dairy sludge in HTC reactor to produce hydrochar used in bioenergy production through electric turbine. The electric energy is considered the main product in this scenario, and the thermal energy recovered from the steam is considered as sub-product.

In the first scenario, a digestate stream containing undigested materials leaves the AD stage with a small portion retained in the AD digester to keep the process alive. The remains go through belt filter to separate the water content from the solid. AD digestate is then utilized in agriculture as fertilizers and the waste activated sludge is dried and stored as a solid fuel. The solid fuel is then combusted in a steam turbine to produce electricity. Heat from the exhaust gas is recovered and used in the continuous heating of the AD digester to ensure mesophilic conditions. In the second scenario, the activated sludge is processed in an HTC reactor before dewatering. Due to the high water content in the AD digestate, there is no need for additional mixing prior to HTC treatment. After that, the solid product is separated from the liquid phase by drying it in a Flo-dry rotary dryer. The acceptable moisture content must not exceed 8% before the electricity generation stage.

Biogas generation potential was calculated theoretically in this section. The theoretical methods implied in this study are based on the elemental composition of the dairy influent. The functional unit (FU) was the treatment and disposal of a 180 tons of dairy effluent per year. Based on the aforementioned facts, the potential biogas production was estimated to be 2523 Nm^3 per year.

Biogas can be converted into mechanical energy through internal combustion engines. However, biogas is a slow burning fuel which require engines with higher compression ratio than the conventional ones. After the spark plug ignites the compressed air and biogas mixture, the burning biogas and air mixture heats rapidly, the expansion forces the piston down to create a torque sufficient to rotate the engine. Then, the engine's exhaust valve opens, releasing the spent air and fuel mixture into the heat exchanger to extract the remaining heat energy. The generator produces the electrical output from the mechanical energy rotating the iron core wrapped in copper wire inside a magnet to create an electrical current. Based on our calculations, a wastewater treatment plant designed to handle 180 tons of dairy effluent per year is eligible to produce up to 4000 kWh in form of electricity, and 5000 kWh in form of heat. Even though the energy value of biogas is lower than the natural gas, biogas is a viable alternative if sufficient amounts were utilized to generate electricity.

To investigate whether HTC of dairy sludge offers an advantage when combined with AD, an energy and mass balance assessment must be evaluated. HTC energy consumption increases with increasing temperatures because of the high energy loss during HTC reactions at high processing temperatures [9]. However, the energy production (output) per unit weight of hydrochar was significantly higher than that of dried raw sludge. The energy output is dependent on the hydrochars' yield and caloric value. Higher energy output is expected at higher HTC processing temperatures due to the higher organic content extracted per kilogram of sludge. On average, less than 10% of the output energy was required as an input energy for the HTC process. This portion does not include the energy required to heat the reactor, nor does it account for heat losses during the process. But with an optimized design and operational procedure, these amounts can be kept to a minimum.

Since the objective of HTC treatment is to replace coal with suitable renewable energy source, hydrochar combustion behavior was evaluated. The organic matter content of sludge decreased after HTC treatment, meaning that the combustion of hydrochars was less violent. However, hydrochar is usually ignited and combusted rapidly which means that coal furnaces are not speculated to ensure the complete combustion of these volatiles, which may lead to further energy loss and undesired emissions. On the other hand, the caloric value of the produced hydrochar was similar to that of sub- bituminous coal, a type of coal is commonly used in electricity production [25].

HTC can recover more energy than slow pyrolysis because it functions under lower temperatures and saturated vapor pressure, avoiding the need to evaporate the water content of sludge. In slow pyrolysis, the moisture content evaporates continuously consuming significant portion of the input energy in the phase change [25]. Thus, despite both chars having combustion behavior similar to that of sub-bituminous coal, hydrochar can offer an alternative to biochar. Even though HTC requires larger fraction of water than that of slow pyrolysis, there is no need for a water addition in case of treating the waste activated sludge due to its high moisture content (85%), but this consideration could differ for wastes with low water content. Other factors must be considered as well, such as the need for high pressure, which increases the complexity of HTC reactor’s design. Other considerations are related to HTC aqueous phase, which can be used as a liquid fertilizer. Finally, and most importantly, more detailed studies and life-cycle analysis are needed to determine the overall environmental footprint of HTC technology, which could play a key role in future research.

6. Conclusion

Different types of wastewater effluent were characterized, based on their COD/BOD_5 ratio and their organic matter content. Results suggested a degradable effluent with high organic content, suitable for AD. However, the extensive observations of COD and BOD_5 measurements show high variation, probably caused by the seasonal variations in the climatic conditions, social customs, water supply characteristics and water availability. Therefore, the correlation should be periodically reevaluated. SCOD release tended to increase significantly after hydrothermal treatment suggesting an efficient pretreatment technique before AD. Still, further investigation is needed to evaluate the technological feasibility of this pretreatment on a large scale, as well as its economic aspect.

Ultrasound assisted microwave disintegration was perceived as an efficient technique for sludge disintegration. The efficiency of ultrasound disruption before microwave treatment was evaluated in terms of the suspended solids (SS) reduction, the chemical oxygen demand removal and the bioenergy recovery. A higher SS reduction and chemical oxygen demand release was observed by ultrasound assisted microwave disintegration when compared to the sole microwave pretreatment. In addition, the combined pretreatment (US + MW) achieved higher methane potential. The energy balance revealed that ultrasound disruption prior to MW disintegration was more profitable than the sole MW pretreatment with net energy production of 26 kWh per kg sludge.

The coupling of HTC and AD was the focus of the third section of this work. Our findings indicated that HTC was suitable in combination with AD from an energy point of view. The physicochemical analyses demonstrated that the produced hydrochar was rich in hydrophilic functional groups and catalytic metal components, favoring higher methane production during AD. Nonetheless, HTC of AD digestate (post-treatment) increased the overall energy recovery and enhanced the performance of biomass steam gasification. Moreover, higher concentrations of macro, micro, and secondary nutrients were detected in HTC aqueous phase, suggesting its suitability for use as a liquid fertilizer. However, the composition and utilization of HTC gaseous products were problematic in the current work, which should be the subject of future research. More information is also needed to assess HTC feasibility for the use on an industrial scale.

The integration of HTC with AD represents an opportunity to improve the energy recovery from sludge when compared to the benchmark process of standalone AD. Furthermore, this strategy is expected to shows a better life cycle environmental performance which could reduce the global warming impact. However, this sensitivity analysis is heavily dependent on hydrochar utilization assumptions. Hydrochar would derive positive effects if utilized to replace fossil fuels, but this is not the case for other biofuels (e.g. biogas).

Also, economic concerns hamper the commercial deployment of this technology, since the calculated treatment cost for the integrated configuration is higher than the conventional anaerobic digestion. The higher cost can be mostly explained from the increased capital investment required which is not compensated by additional revenues, given the current market value of hydrochar. Nevertheless, the economy of scale, and the potential improvement of hydrochar yield, along with its consideration as renewable fuel, could improve the overall economic potential of HTC. The changing regulatory framework around waste sludge on nutrient recovery will probably influence the prospective market of hydrochar produced from hydrothermal treatment of sludge, which has been proven as an environmentally-sensible route for sludge treatment.

7. Summary

In this Ph.D. dissertation, I have investigated several pre and post treatment techniques to enhance the anaerobic digestion (AD) within the wastewater treatment domain. The evaluation was based on energy and resource recovery through biofuel and bio-fertilizer generation.

In the introduction part, an overview about the wastewater treatment and pollution issues was given, including the problems related to the excess discharge of sludge intense nutrients to water bodies. I also have given a brief introduction about the previously investigated pre and post treatment techniques, focusing on the energy and nutrient recovery, empathizing the fact that the integration of hydrothermal pretreatment with AD represents an opportunity to improve the energy recovery from sludge when compared to the benchmark process of standalone AD. Furthermore, this strategy is expected to show a better life cycle environmental performance which could reduce the global warming impact. The literature review was useful in synthesizing information about the important concepts of coupling AD with US, HTC and MW from different aspects, including their benefits and limitations, and identifying sectoral knowledge gaps that are common across this research area. The literature review covered topics related to wastewater treatment globally and in a regional status, as well as topics related to sludge biodegradability and biogas production, and types of anaerobic reactors and the parameters affect biogas production during AD.

Driven by the necessity and need of more information regarding the energetics of coupling AD with other pretreatment technologies, I designed different experiments to evaluate the efficiency of coupling AD with other treatment techniques. After sludge sampling and collection, the dairy effluent was chosen to have the best potential for AD based on its COD/BOD_5 ratio and sludge biodegradability compared to those of municipal and meat processing wastewater. However, the extensive observations of COD and BOD_5 measurements showed high variation, probably caused by the seasonal variations in climatic conditions, social customs, water supply characteristics and water availability. Therefore, the correlation should be periodically reevaluated. In summary, SCOD release tended to increase significantly during hydrothermal treatment suggesting an efficient treatment prior to AD. However, further investigation was still needed to evaluate the technological feasibility of such a treatment.

After wastewater characterization, US disruption of sludge was employed prior to MW disintegration. US assisted MW disintegration was perceived as an efficient technique prior to AD. The efficiency of this combined treatment process was evaluated in terms of suspended solids (SS) reduction, chemical oxygen demand (COD) removal and bioenergy recovery. A higher SS reduction, COD removal and methane potential was achieved by the combined pretreatment (US + MW). The energy balance calculations proved that US disruption prior to MW disintegration was more profitable than the sole MW pretreatment with net energy production of 26 kWh per kg sludge compared to 18 kWh per kg sludge, respectively.

In the second approach, HTC was employed as pre and post treatment to AD. Our results indicated that the integration of HTC with AD represents an opportunity to improve the energy recovery from sludge when compared to the benchmark process of standalone AD. The findings of this study indicated that HTC is suitable in combination with AD from an energy point of view. The physicochemical analyses demonstrated that hydrochar was rich in hydrophilic functional groups and catalytic metal components, favoring higher methane production during AD by 300 mL/gCOD compared to raw sludge. Nonetheless, HTC of AD digestate (post-treatment) increased the overall energy recovery and enhanced the performance of biomass steam gasification resulting in higher syngas production (1.543 Nm^3/kg for hydrochar compared to1.02 Nm^3/kg for raw sludge). Moreover, higher concentrations of macro, micro, and secondary nutrients were detected in HTC aqueous phase, suggesting its suitability for the use as a liquid fertilizer. The composition and utilization of HTC gaseous products were problematic in the current work, which should be the subject of future research. More information is also needed to assess HTC feasibility for the use on industrial scale.

The changing regulatory framework around waste sludge will probably influence the prospective market of the produced hydrochar. Hence, the following points must be addressed in any future research:

- The correlation of all measurements related to wastewater quality should be periodically reevaluated to address the variations caused by changes in climatic conditions, social customs, water supply characteristics and water availability.
- The effect of MW pretreatment should be studied in depth to evaluate its athermal effect.
- HTC economy of scale, and the potential improvement of hydrochar yield, along with its consideration as renewable fuel should be further investigated to assess the potential use of HTC on industrial scale.
- Investigation of the capital investment cost of HTC implementation.
- A life cycle analysis to assess HTC environmental footprint.

8. Összefoglalás

PhD értekezésemben számos elő- illetve utókezelési technikát vizsgáltam meg a szennyvizek anaerob lebontásának (AD) céljából. Az egyes technikák értékelése az előállított bioüzemanyag és műtrágya energia-, erőforrás-, valamint biomassza hasznosításán alapult.

A bevezető részben áttekintést adtam a szennyvízkezelésről és a szennyezésekről, ideértve a tápanyagban gazdag iszapok túlzott kibocsátást. Emellett röviden bemutattam az energia és tápanyag visszanyerésre fókuszáló, ismert elő- és utókezelési kutatásokat. A szakirodalomban néhány esetben már bizonyítást nyert, hogy a hidrotermikus előkezelés az anaerob lebontással történő közös alkalmazása lehetőséget jelent az iszapból történő energia-visszanyerés javítására, továbbá ez a stratégia várhatóan jobb életciklus-környezeti teljesítménye miatt csökkentheti a globális felmelegedés hatását.

A szakirodalmi áttekintés hasznosnak bizonyult az anaerob lebontás (AD) a hidrotemikus karbonizáció (HTC) és mikrohullámú enregia bevitel (MW) különböző szempontokból történő összekapcsolásában, valamint azok előnyeinek és hátrányainak megismerésében, és segített a kutatási területek hiányosságainak, a még hiányzó ismeretek felismerésében. A szakirodalmi áttekintés témakörei a globális és regionális szennyvízkezelési módszereket épp úgy lefedik, mint az iszaplebontás, a biogáztermelés, az anaerob reaktorok és a biogáz termelését befolyásoló paraméterek hatásának kérdéseit.

A minél több, értékes és hasznosítható információ megszerzése érdekében, munkám során számos kísérletet végeztem a különböző előkezelésekkel összekapcsolt AD energia termeléséhez kapcsolódóan. Az iszapminták begyűjtése és elemzése alapján a tejipari minták bizonyultak a legelőnyösebb alapanyagnak az AD vizsgálatokhoz a magas kémiai- és biokémiai oxigénigény arányuk miatt (COD/BOD5), szemben a kommunális ill. húsipari szennyvízmintákkal.

Az egyes minták COD és BOD5 értékeinél nagyobb eltérések mutatkoztak, az évszakok, a klimatikus körülmények, a vízfogyasztási karakterisztika, a vízellátási jellemzők függvényeként, emiatt az összefüggések ismételt felülvizsgálata szükséges.

A kapott eredmények összefoglalva elmondható, hogy az oldott kémiai oxigénigénye (SCOD) jelentősen megnőtt a hidrotermális kezelés során, és a maximális koncentrációt 225 °C-on (6 perc) érte el, ami az AD előtti hatékony kezelésre utal. Azonban további vizsgálatokra volt szükség az ilyen tipusú kezelés technológiai megvalósíthatóságának értékeléséhez.

A mikrohullámú lebontást megelőzően az iszap mintákat ultrahangos roncsolásnak vetettem alá. Ennek a kombinált kezelési eljárásnak a hatékonyságát a lebegő szilárd anyagok (SS) és a kémiai oxigénigény (COD) csökkenése valamint a bioenergia visszanyerésének szempontjából értékeltem. A kombinált előkezelés (US + MW) nagyobb SS-csökkentést, COD-eltávolítást és metánpotenciált eredményezett. Az energiamérleg-számítások bebizonyították, hogy a mikrohullámos kezelést megelőző ultrahangos roncsolás jövedelmezőbb, mint az önálló mikorhullámos előkezelés, vagyis 26 kWh/kg iszap nettó energiatermelést eredményez a 18 kWh/kg iszappal energiával szemben.

A második megközelítési módszernél hidrotermikus eljárást (HTC) alkalmaztam az AD előtti és utáni kezelésként. Eredményeim azt mutatták, hogy az anaerob lebontás HTC kezelésekkel történő összekapcsolása szintén kiaknázható lehetőséget kínál az iszapból történő energia-visszanyerés javítására, összehasonlítva az önállóan végzett AD folyamattal, vagyis energetikai szempontból eredményt érhetünk el a két kezelés kombinálásával. A fiziko-kémiai elemzések kimutatták, hogy a keletkezett bioszén gazdag hidrofil funkciós csoportokban és katalitikus fém összetevőkben, ami nagyobb metán termelődést eredményez az AD során (192%-kal magasabb a hozam nyers iszaphoz képest). Az AD-t követően alkalmazott HTC utókezelés növelte tehát az általános energia-visszanyerést és javította a biomassza gáztermelésének teljesítményét 1,543 Nm3/kg értékre, a nyers iszap alkalmazásánál mérhető 1,02 Nm3/kg értékkel szemben. Ezen kívül a HTC vizes fázisában a makro-, mikro- és másodlagos tápanyagok magasabb koncentrációban vannak jelen, ami arra utal, hogy alkalmas lehet folyékony műtrágyaként történő felhasználásra.

A jelenlegi munkában a HTC gázfázisú termékeinek összetételének meghatározása és felhasználásuk sajnos gondot okozott, ami a jövőbeni kutatások tárgyát kell, hogy képezze, valamint további információra van szükség a HTC ipari méretekben történő alkalmazhatóságára is. A hulladék-iszap körüli változó szabályozási környezet, valószínűleg hatással lesz az előállított bioszén leendő piacára kedvező szabályozási tendenciák esetében, ezért a jövőbeli kutatás során a következő kérdésekkel célszerű foglalkozni:

- A szennyvízminőséggel kapcsolatos mérések korrelációját időszakonként újra kell értékelni, hogy figyelembe vegyük az éghajlati viszonyok, a fogyasztói szokások, a vízellátási jellemzők és a víz elérhetősége miatt bekövetkező változásokat.

- A MW előkezelés hatását a MW atermikus hatásának szempontjából is tanulmányozni szükséges.

- A HTC gazdaságosságát és a bioszén hozam lehetséges javítását, valamint a megújuló üzemanyagként történő alkalmazhatóságát vizsgálni kell a jövőben a HTC ipari méretű alkalmazhatóságának érdekében.

- HTC beruházási költségének vizsgálata.

- Életciklus-elemzés a HTC környezeti lábnyomának felméréséhez.

9. New Scientific Results

1) MW disintegration enhanced the release of secondary, micro and macro nutrients to the aqueous phase, increasing the overall nutrient recovery and sludge solubility.

The concentrations of all measured parameters showed higher solubility into the aqueous phase after the pretreatment process (Table 16). Higher concentrations of macronutrients such as N, P and K, Cu and Mg was reported due to the hot water leaching. Hence, MW irradiation decreased the values of the SAR due to the higher recovery of Mg and Ca after MW disintegration. Another indication of the higher solubility of the dairy sludge after MW disintegration was the increase in DOC concentrations.

2) It was confirmed that sludge disruption via US prior to MW disintegration is a cost effective and feasible process prior to anaerobic digestion.

In the case of sludge with a high organic content such as the dairy sludge, it was proven that US treatment was able to increase sludge solubility by 15% with a 30% reduction in the energy consumption compared to sole microwave treatment, resulting in a 28% increase in biogas production.

3) Maximum sludge solubilization in dairy sludge (SCOD/TCOD) was higher in case of ultrasonic treatment prior to MW disintegration.

Sludge solubilization increased from 0.07 ± 0.01 to 0.12 ± 0.01 in flocculated sludge, and from 0.09 ± 0.01 to 0.15 ± 0.01 in deflocculated sludge subsequent to MW disintegration.

4) It was proven that hydrothermal pretreatment (HTC) of dairy sludge increased methane production during AD.

No study as of yet evaluated the use of hydrochar to enhance biogas production during AD. In this work, higher biogas production was obtained after HTC pretreatment, which was a clear indicator of the increased availability of the organic substrates within the biomass, leading to an enhanced conversion of the organics during methanogenesis (methane production). The amount of biogas produced, in terms of ml/gCOD was higher by 192% compared to that of raw sludge (at 210 °C HTC processing temperature).

5) Hydrothermal carbonization (HTC) improved the fuel quality of the waste activated sludge.

During HTC, dairy sludge digestate evolved progressively from compositions falling within the range of biomass, peat, and lignite to a material that is closer in composition to coal. This evaluation was based on literature using *Van Krevelen diagram,* which proved that HTC improved the fuel quality of raw dairy sludge and digestate (Figure 13).

6) HTC improved biomass steam gasification by increasing H_2 production compared to raw sludge.

The H_2 content of hydrochar was significantly higher than that of dairy sludge at the same temperature and for the same S/B ratio. Gas yield from steam gasification of dairy sludge was about 1.02 Nm^3/kg compared to 1.543 Nm^3/kg for hydrochar. HTC-derived hydrochar is rich in hydrophilic functional groups. Therefore, it is dispersed easily in the water molecules during steam gasification. Thus, a higher amount of unbound H atoms was generated during hydrochar steam gasification compared to that of raw sludge. Additionally, the increased metal content in the produced hydrochar could be another reason for the higher gasification reactivity and conversion efficiency.

10. Publications

MTMT identifier: 10066622, ORICID: 0000-0001-9585-5228, Citations (up to date): 13.

- Al Ramahi, M., Keszthelyi-Szabó, G., & Beszédes, S. (2021). Coupling hydrothermal carbonization with anaerobic digestion: an evaluation based on energy recovery and hydrochar utilization. Biofuel Research Journal, 8(3), 1444-1453. (Q1, IF: 6.9)
- Al Ramahi, M., Keszthelyi-Szabó, G., & Beszédes, S. (2020). Improving biogas production performance of dairy activated sludge via ultrasound disruption prior to microwave disintegration. Water Science and Technology, 81(6), 1231-1241. (Q2, IF: 1.9)
- Al Ramahi, M., Beszédes, S., & Keszthelyi-Szabó, G. (2020). The effect of hydrothermal treatment on industrial wastewater: Hungary as a case study. Progress in Agricultural Engineering Sciences,16 (S1), 45–51. (Q3).

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- Al Ramahi M;, Beszédes S; Keszthelyi-Szabó, G. *Evaluation of physicochemical properties of waste activated sludge.* In: Gábor, Rákhely; Cecilia, Hodúr (eds.) II. Sustainable Raw Materials Conference Book - International Project Week and Scientific Conference. Szeged, Hungary: University of Szeged (2019) 312 p. pp. 51-54. , 4 p. International Conference on Science, Technology, Engineering and Economy. Szeged, Hungary.
- Al Ramahi M;, Beszédes S; Keszthelyi-Szabó, G. *Biodegradability of activated sludge: the role of microwave irradiation pre-treatment on the sludge solubility, dewaterability and potential biogas production.* In: Pappné, Sziládi Katalin; Bíró, István; Beszédes, Sándor; Gál, József; Hampel, György; László, Zsuzsanna; Deák, Dalma; Kiss, Magdolna; Imre, Fodor Gabriella; Mihalkó, József (eds.) Műszaki, technológiai és gazdasági kihívások a 21. században című konferencia nemzetközi magyar nyelvű tudományos konferencia: előadások és poszterek összefoglalói. Szeged, Hungary: University of Szeged Faculty of Engineering (2019) 139 p. p. P31 , 1 p. Scientific.
- Al Ramahi M;, Beszédes S; Keszthelyi-Szabó, G. *BIODEGRADABILITY OF ACTIVATED SLUDGE: THE ROLE OF MICROWAVE IRRADIATION PRE-TREATMENT ON THE SLUDGE SOLUBILITY AND POTENTIAL BIOGAS PRODUCTION.* In: Gábor, Rákhely; Cecília, Hodúr; Balázs, Lemmer; Zoltán, Jákói

(eds.) II. Sustainable Raw Materials International Project Week And Scientific Conference: Book of Abstracts. Szeged, Hungary: University of Szeged (2019) 76 p. pp. 16-16. , 1 p. Scientific.

- Al Ramahi M;, Beszédes S; Keszthelyi-Szabó, G. *Biodegradability and Characterization of Industrial Wastewater in Hungary.* In: Viktória, Zsom-Muha (eds.) 2nd International Conference on Biosystems and Food Engineering in memory of Professor András Fekete. Bp, Hungary : Szent István Egyetem, Élelmiszertudományi Kar (2018) Paper: E212 , 7 p. REAL SZTE Publicatio. Scientific.

- Al Ramahi M;, Beszédes S; Keszthelyi-Szabó, G. *Impacts of microwave pretreatments on the anaerobic digestion of dairy waste activated sludge.* In: István, Bíró; Sándor, Beszédes; József, Gál; György, Hampel; Szabolcs, Kertész; Mária, Szabó; Katalin, Sziládi (eds.) International Conference on Science, Technology, Engineering and Economy: ICOSTEE 2018 : Book of Abstracts. Szeged, Hungary: University of Szeged Faculty of Engineering (2018) 87 p. pp. 36-36. , 1 p. Scientific.

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