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

“Ph.D. Thesis Booklet”

By

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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).

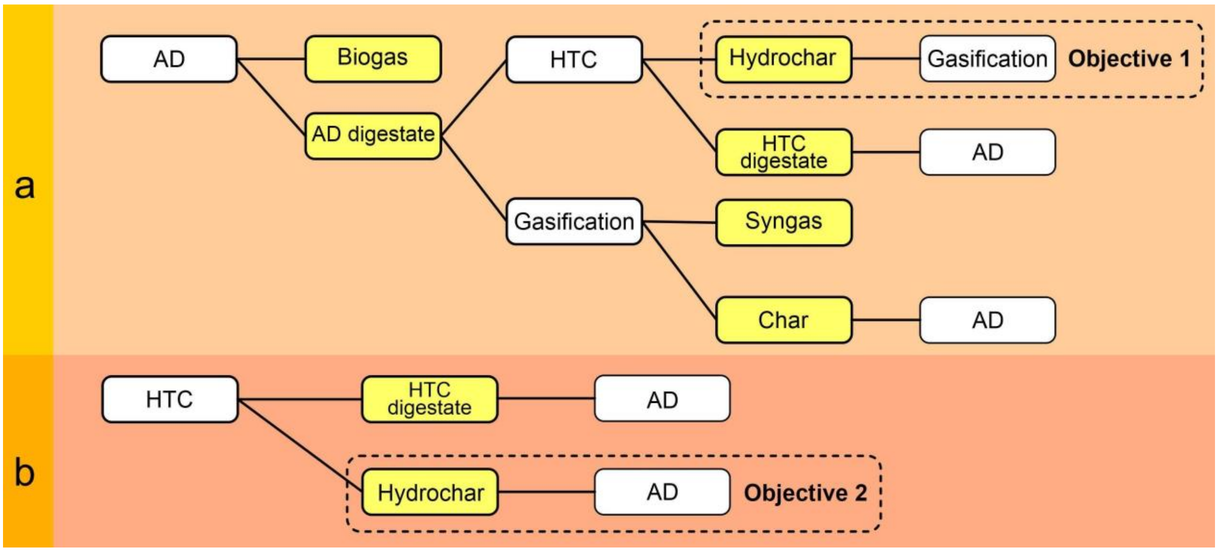

Figure 1. *A schematic diagram representing (1) HTC post-treatment and (2) HTC pretreatment to AD.*

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.

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.

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.

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.

List of Publications

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- 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).

Conferences presentations

- Al Ramahi M;, Beszédes S; Keszthelyi-Szabó, G. Study to evaluate the effect of ultrasonication prior to microwave disintegration on anaerobic digestion of dairy sludge. In: Alapi, Tünde; Ilisz, István (eds.) Proceedings of the 25th International Symposium on Analytical and Environmental Problems. Szeged, Hungary : University of Szeged (2019) 464 p. pp. 50-53. , 4 p.25th International. Symposium on Analytical and Environmental Problems. Szeged, Hungary.
- 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.
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- 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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