Life Cycle Assessment of Processing Biogenic Residues Via Anaerobic Digestion Coupled with Hydrothermal Carbonization

By

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MASTER OF SCIENCE IN ENGINEERING

(CHEMICAL)

Department of Chemical Engineering

BANGLADESH UNIVERSITY OF ENGINEERING

AND TECHNOLOGY, DHAKA

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Abstract

Bangladesh produces an astounding amount of around 52.8 million tonnes of agricultural waste annually. Anaerobic digestion (AD) has been traditionally used for processing biogenic residues in Bangladesh, however, the inadequate handling of digestate slurry as by-product is a major flaw of this system. Rich in nutrients (nitrogen, phosphorus, calcium etc.) and organics, digestate is difficult to handle in its slurry form and may cause environmental pollution, hindering efficacy of AD.

Hydrothermal carbonization (HTC) is an emerging technology for upgrading low-quality and high moisture biomass to carbonaceous material called hydrochar at moderate temperature and pressure-a suitable means for recovering nutrients from organic waste. For Bangladesh, integration of AD with HTC has excellent potential for co-producing biomethane and biofertilizer, however no study evaluated the environmental implications of such integration.

In this study, the mentioned gaps were addressed in two ways-employing hydrothermal carbonizations of AD-digestate for the characterization of hydrochar and conducting life cycle assessment (LCA) comparing a standalone AD system (anaerobic mono-and co-digestion) with proposed AD-HTC integration for evaluating environmental implications. Five impact categories, such as Climate Change, Eutrophication Potential, Acidification Potential, Terrestrial/Human Toxicity, and Malodor emissions were determined. For anaerobic digestion technologies, life cycle impact assessment revealed co-digestion yielded better environmental performance than mono-digestion by reducing climate change (117%), eutrophication potential (54.5%) and terrestrial toxicity (55.7%), however the key hotspot for both was open storage of digestate. AD-HTC system however performed significantly better by reducing all of the impacts compared with standalone AD system with the highest reductions occurring for ecotoxicity and eutrophication potential. Process water from HTC was found to be a key pollutant for AD-HTC system, thus requiring post treatment in the form of nutrient recovery.

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Chapter 1

INTRODUCTION

1. INTRODUCTION

Waste management is a growing concern for developing countries such as Bangladesh which has a high number of populations with a growing economy. In 2014, Bangladesh generated about 22.98 million tonne of organic waste, which by now should significantly increase [1], with a per capita waste generation rate of 0.56–0.7 kg/day. More than 70% of solid waste produced contains biogenic residues of various origins, such as livestock manure, agricultural residues, food waste etc.- also known as agricultural residues [2]. Majority of agricultural waste in Bangladesh either gets lost during production or landfilled, causing environmental concerns. The decentralized nature of its origin and production as well as high moisture content of these waste make it difficult to be treated directly via thermochemical treatments. As a result, common and easy to deploy biological treatment methods such as anaerobic digestion has emerged as viable options for reducing waste volume while simultaneously producing a renewable energy carrier such as biogas. Because of its simplicity and low cost, anaerobic digestion has gained traction in developing countries such as Bangladesh and have been operating since 2002 [3], [4].

Anaerobic digestion (AD) of biogenic waste is a long-standing and important technology for waste reduction and renewable energy generation. Biogas and digestate are the primary byproducts of anaerobic digestion. The latter has the potential to be used soil amendment. Despite the apparent benefits of AD, the diffusion of this technology in Bangladesh has been very slow even after being introduced decades ago. Anaerobic digestion has several inherent disadvantages. There are several barriers to anaerobic digestion of single substrates, also known as mono-digestion, including insufficient organic loading and a C/N ratio that leads to the formation of inhibitors, lowering biogas yield [5], [6]. While co-digestion has been reported to be both technically and environmentally

sustainable compared to mono-digestion, both technologies struggle with destabilization of the substrate.

One of the main reasons behind the reluctance towards adoption of anaerobic digestion technologies in Bangladesh is handling of digestate slurry. While AD can be utilized for treating waste, it simultaneously creates a waste stream- which is the nutrient rich digestate slurry. Typically, this slurry is utilized as a biofertilizer in many countries via other stabilization processes such as composting. However, various studies reported that digestate compost may cause overt nutrification of the soil and hence be detrimental to be used as a soil amendment material. Moreover, in Bangladesh, there are legal constraints against using liquid fertilizer directly to the soil, hence many biogas plant owners dispose of the digestate slurry in landfills or store in open ponds. This typical handling of digestate slurry creates several nuisances, extending to serious health concerns.

Post treatment of digestate is thus required to mitigate the environmental concerns of AD systems. In recent years, hydrothermal carbonization (HTC) has emerged as a suitable technology for treating high moisture waste streams. HTC requires water and organic matter, to break it down to a solid carbonaceous product called hydrochar and a liquid effluent or process water. Hydrochar is a densified solid hydrophobic product rich in C, thus making it suitable for varied applications such as fuel, soil amendment, CO_2 capture etc. Digestate, which is also an organic waste with high moisture, treating it via HTC emerged as a potential option for valorization. However, there have not been sufficient studies which evaluate the integration of HTC with AD from environmental perspective and no studies have been conducted in the context of Bangladesh.

In this study, we aimed to address the mentioned gaps by conducting a life cycle assessment of anaerobic digestion system as a standalone and coupled with HTC to evaluate their

environmental implications. In addition, we synthesized hydrochar from local biogenic residues and characterized their compositional parameters. In Chapter 2, we first delve into the existing literature on the current state of waste management in Bangladesh and the potential of HTC as a viable technology for treating digestate. Chapter 3 focuses on the experimental methods applied for synthesis and characterization of hydrochar and life cycle assessment methodology for environmental assessment. Chapter 4 discusses the results of life cycle assessment and chapter 5 draws important insights and recommendations from the study.

Chapter 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1. Agricultural Waste in Bangladesh: Generation and Fate

Agricultural waste comprises the largest share among different waste streams for Bangladesh, owing to being an agricultural country. Agricultural waste can be defined as biogenic residues originating from agricultural practices, thus including mainly three types of residues-process-based crop residues, field-based crop residues and livestock waste [7]–[9]. Few studies reported that around 70% of the total waste contain agricultural biogenic residues[8], [9]. A 2017 study by Rahman et al. determined the annual agricultural waste to be around 58 million tons [8]. Considering a waste generation rate of 0.74 kg per day/person, it is predicted that by 2050 agricultural waste generation could amount to be 9320 billion tons per year [7]. Managing this huge amount of agro-waste has imposed several concerns, primarily because the current management of such waste is not efficient.

Unlike OFMSW, agricultural waste is generated in a decentralized manner. Thus, recovering such waste becomes difficult. In fact, one study reported that a major fraction of the process-based crop residues is recovered while field-based residues perish through burning or rotting in the field[10]. On the other hand, livestock residues are typically handled in farm-scale treatment technologies such as biogas generation, used as feed, compost, or landfilled [10].

As mentioned in the previous section, biogenic residues are potential fuel feed of the future. Agricultural biogenic residues contain a considerable amount of recoverable energy. It is estimated that around 223 PJ per year from theoretical considerations [8], [11]. Although several factors such as moisture content was not considered. In Table 1, a summary of the types, characteristics and energy potential of the agricultural waste in Bangladesh is shown.

As aforementioned, agricultural waste can be crop-based (process and field-based) and livestock residues. These two types of waste vary greatly in their properties. However, in general, majority of agricultural residues have few common characteristics. Firstly, agricultural residues tend to be of high moisture at the range of containing 70 to 80% moisture content. Crop residues contain a higher amount of fixed carbon than livestock waste with relatively lower moisture[12]–[14]. However, agricultural residue tends to contain higher ash content, thus making energy recovery difficult.

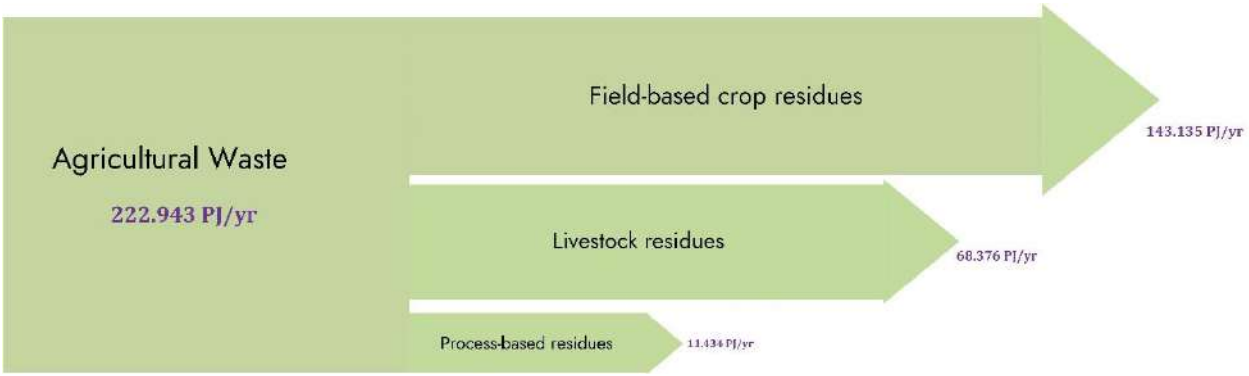


Figure 1. Agricultural waste types in Bangladesh and their energy potential

Due to the decentralized generation of agricultural waste, majority of crop-based residues in Bangladesh are lost at various stages of production. Field-based crop residues typically decompose, with the loss ranging from 29% to 100%.[8] Process-based crop residues, however, have higher recovery of up to 100% [8]. A small fraction of crop residues is utilized as cooking fuel and feed in the farms[8]. Collection of agricultural residues is one of the biggest challenges in the path of overall management. In some cases, the waste produced is sent to landfills, especially if the waste generated from semi-rural or urban areas. Livestock waste such as poultry litter, and cow manure are usually produced from farms. Currently, a fraction of farm produced manure is treated via anaerobic digestion in local biogas plant.

Table 1. Total available amount, biogas potential and energy potential of agricultural residues in Bangladesh [8]

Type of waste		Total available amount (million tons)	Biogas Production Potential (m^3/kg VS)	Biogas Production per year (million m^3)	Energy Potential (TJ/year)
Animal waste	Buffaloes	0.7	0.3	160	3670
	Cattle	12.3	0.2	2295	52,777
	Goats	1.5	0.3	282	6486
	Poultry	0.2	0.3	67	1533
	Sheep	2.1	0.2	170	3901
	Total	17		2974	68,374
Process-based Crop residue	Rice bran	1.9	-	313	7207
	Sugarcane	0.2	-	27	624
	Coconut husks	0.2	-	39	901
	Maize cobs	0.5	-	76	1745
	Maize husks	0.2	-	37	845
	Groundnut husks	0.03	-	5	113
	Total	3		497	11,434
Field-based crop residue	Rice straws	29.5	-	4859	111,763
	Wheat straws	0.2	-	50	1156
	Jute stalks	3.9	-	624	14,345
	Pulses straws	0.1	-	17	382
	Cotton stalks	0.1	-	15	355
	Maize stalks	2.8	-	436	10,035
	Ground nut straws	0.06	-	10	237
	Vegetables	1.0	-	140	3209
	Sugarcane tops	0.8	-	71	1653
	Total	38	-	6222	143,135

2.1.1. Anaerobic Digestion: Experience in Bangladesh

Anaerobic digestion (AD) is a process where organic matter breaks down to mainly biogas (CH_4, CO_2) and slurry remain called digestate, in anaerobic condition [15]–[17] . The process is applied in biogas plants, where the main product biogas is utilized as an energy carrier. AD is a mature technology world-wide, attaining a technological readiness level (TRL) of 9. One of the main advantages of this technology is the ability to handle high moisture and high ash biomass. Since anaerobic digestion require a slurry feed, biogenic residues with high degradability and moisture can be readily treated via AD. Moreover, this technology can be implemented in decentralized manner, thus making it a suitable alternative of landfilling for agricultural residues.

In Bangladesh, anaerobic digestion has been implemented for two decades [9]. The first biogas plant in Bangladesh was constructed in 2002 and since then both government and non-governmental efforts led to making biogas plants a common technology [9], [18]. IDCOL began its biogas program in 2006 with other organizations such as German Technical Cooperation (GIZ) and World Bank and constructed over 34,000 biogas plants[18]. Table 2 summarized the total number and types of biogas plants installed by different organizations in Bangladesh. Currently, there are around 100,000 biogas plants installed all over the country of different plant size, majority being community sized biogas plants [18]. Most of these biogas plants can be categorized as community sized or farm-scale biogas plants. Livestock waste, such as manure, are typically utilized as the main source of waste feed for these plants, hence they are simultaneously called farm-scale biogas plant. This arrangement of biogas plants proved to be beneficial for Bangladesh for waste management, as it has large amount of dairy

and poultry farms [13], [19]–[21]. Studies suggest Bangladesh has over 150,000 poultry farms, producing an undefined amount of poultry litter which needs to be managed properly [10].

Table 2: Biogas installation by different organizations [21]

Organization	Number of Plants in 2013	Number of Plants in 2015
IDCOL	31,258	35,000
BCSIR	22,334	23,000
Grameen Shakti	7200	8000
NGO and others	9850	11,530

2.2.Challenges of Implementing Anaerobic Digestion in Bangladesh

Despite the efforts to establish anaerobic digestion as one of the primary waste management technologies in Bangladesh for treating problematic agricultural residues such as livestock waste, the current state of this technology is in dire need of improvement. A recently published study report by SREDA noted that among the 100,000 installed biogas plants, only 130 biogas plants are operational in 2018, which is around 0.1% of the stated capacity [18]. Hence, despite being an established technology, AD has failed to get momentum to become a leading waste management route for high moisture agricultural residues such as livestock waste.

There are mainly three main limitations of properly implementing AD technology in Bangladesh [9], [18], [21]. Firstly, the operational cost for running a biogas plant is high. Operational cost, labour cost and maintenance costs constitute around 35% of the total investment for a medium scale biogas plant [22]. Handling of waste streams from farms to

biogas plants and utilizing biogas for energy production requires continuous financial strain to farm owners, especially for developing countries such as Bangladesh [10].

Secondly, biogas production is a slow process, which can take up to around 7 days for a feed to anaerobically digested. Unlike natural gas systems, biogas systems are not as efficient. Small scale biogas plants in Bangladesh succeeded the least due to this limitation. Moreover, the quality of biogas as a product gas is low. Containing around 50% CO_2, the energy content of biogas is very low. Moreover, biogas also contains trace gases such as NH_3 and H_2S, the latter making the post usage of biogas very difficult due to strong odour and potential corrosion of downstream equipment.

Lastly, the handling of digestate was found to be a major reason behind the slow diffusion of anaerobic digestion technologies in Bangladesh. Digestate slurry from anaerobic digester mainly contain organic fraction and nutrients from the feed. Majority of digestate slurry is kept at open storage adjacent the biogas plant while a small fraction is sold as biofertilizer. The application of latter is not common, as utilization of liquid fertilizer has legal constraints in Bangladesh. At slurry from, the digestate remain at an unstable stage, thus causing significant environmental implications if used. Nutrients in unstable form may cause over nutrification of the soil, hence causing adverse environmental effects such as eutrophication [23]. According to SREDA, most of the farm-scale biogas plant owners reported disposing the digestate slurry into the open storage [18]. Depending on the feed of the anaerobic digestion feed, the quality of digestate slurry vary significantly [24]–[26]. Hence, the quality of digestate slurry varies greatly depending on the type of feed being utilized. Landfilling and open storage both cause greenhouse gas emissions, thus proper handling of digestate slurry is required for sustainable deployment of efficient biogas production systems.

Despite the limitations of current biogas production systems in Bangladesh, this technology remains a vital step towards adopting renewable energy generation locally. Aside from utilizing biogas as the product, digestate slurry could also be upgraded to a stable fertilizer form- providing both environmental and economic benefits [25], [27].

2.3.Digestate Valorization: State-of-the-art Perspectives

Digestate is a by-product of typical anaerobic digestion, containing unconverted remainder of the feed. Management of this by-product, however, remains in dire situation. However, this digestate contains valuable nutrients which could be recovered in post treatment. In this section, digestate as a potential resource would be explored and the typical management.

2.3.1. Digestate Characteristics: Potential Feedstock

Digestate contains the remainder solid after anaerobic digestion, which contains the by-products of microbial degradation as well as the undigested feed [28]. Thus, the property of digestate depends largely on the type of feed stock being digested and the operating conditions. The organic matter content and total organic carbon contents of a digestate vary greatly depending on these two factors. For instance, in a case where the feedstock has high amount of organic matter but short hydraulic retention time (HRT), the digestate end up containing high amount of degradable organic carbon [29]. According to few studies, generally 35% of the total organic matter remain in the digestate, a fraction of which later degrades to residual CH_4 and CO_2 during open storage or landfilling [30], [31]. Often at farm scale plants, digestate contains both manure and bedding materials used while rearing farm animals.

Digestate also contains the major portion of the micronutrients in the feed. These micronutrients are mainly trace metal elements from the feed crops or vegetables fed to animals or directly digestated in the anaerobic digester. Typically, Zn, Cu and Pb were commonly found from anaerobic digestate derived from animal manure such cow or poultry manure [30].

Digestate from other more heterogenous waste streams such municipal solid waste (MSW) often may contain other metal elements such as Cd, Cr, Ni, As etc. [30]. The presence of nutrients in the digestate make it suitable for soil applications, however the trace metal elements confirm that there are risks involved in direct application of digestate without reducing the bioavailability of these trace metals into the environment. Moreover, in some cases, considerable amount of antibiotic concentrations were found in the digestate which made the direct application of it in the soil concerning. Studies reported that antibiotic concentrations were found in both the solid and liquid fractions of digestate [29].

2.4.Digestate Valorization: Biological Routes

2.4.1. Composting

Composting is a common method to biologically stabilize the digestate slurry into a biofertilizer [32], [33]. Contrast to anaerobic digestion, during composting the organic matter degrades in aerobic conditions and reduces phytotoxicity and pathogens [23], [26]. The operating conditions of composting are adjusted to minimize the loss of N and C losses from the feed. Typically, during composting, digestate is mixed with different types of biomass as bulking agents to increase its nutrient contents.

Composting is the most common method of treating digestate. However, it has several bottlenecks such as lower bio-degradability, high moisture and low C/N ratio [30].The low C/N ratio results in an unstabilized mixture and may cause nitrogen loss, thus decreasing the fertilization quality of the compost [30]. Rehl and Müller reported ammonia emissions during composting, which ranges to 20% of total ammoniacal nitrogen in the feed and nitrous oxide which is around 1.4% of total nitrogen and methane emission up to 8% of carbon for a 10-week

composting[29]. Composting quality greatly depends on the parent feed, thus varying in quality greatly.

2.4.2. Enzymatic Hydrolysis

Hydrolysis by enzyme Using specific enzymes, this process converts bio-macromolecules (such as proteins and polysaccharides) into simple monomers (such as amino acids and sugars) (such as proteases and cellulases). Animal manure fibers contain lignin, hemicellulose, and cellulose. During anaerobic digestion, only hemicellulose and, to a lesser extent, cellulose are consumed.[30]. This causes the fiber structure to be partially or completely broken down, increasing the hydrolysability potential of the fibers in the digested manure. Undecomposed fibers, like corn stover and switchgrass, are a high-quality cellulosic feedstock. Furthermore, it is not subject to seasonal fluctuations, and there is no requirement to collect and stockpile large quantities of raw material to ensure its availability throughout the year. To increase the sugar yield during enzymatic hydrolysis, digested manure can be treated chemically, particularly with sodium hydroxide. Digested manure also contains a number of nutrients required for sugar fermentation with yeasts or bacteria. The removal of lignin may increase cellulose hydrolysis, and the lignin recovered after lignocellulosic fermentation has a high potential for fermentative valorization due to its higher heating value (from 21.5 to 23.5 MJ/kg – dry basis) [30].

2.5.Thermochemical Treatment

2.5.1. Gasification

Gasification is a thermochemical process in which carbonaceous feedstock is converted into primarily gaseous products rich in CO, H_2, and tar via a series of heterogeneous and homogeneous high-temperature reactions [34]–[36]. The fuel particle is dried, pyrolyzed, and then subjected to solid-solid and gas-solid reactions, resulting in a non-condensable gas and a complex liquid by-product-tar. The gas's product distribution is affected by a number of factors, including operational temperature, feedstock properties, and gasifying agents [37]–[40]. The gasification medium or gasifying agent used would be determined by the desired composition of the product gas [40]–[42].

2.5.2. Pyrolysis

Pyrolysis is a promising treatment method for solid digestate. Pyrolysis is an endothermic process that releases volatile matter from organic matter to produce a densified carbonaceous product known as biochar[43], [44]. It can treat any carbon-based material, regardless of its biodegradability. Pyrolysis can be classified as "slow" or "fast" depending on the operational conditions[45]. Slow pyrolysis generally occurs at low heating rates (10 °C min-1) and residence times of minutes or hours, whereas fast pyrolysis occurs at high heating rates (1000 °C min-1) and residence times of seconds or minutes. Slow pyrolysis generally produces char (35 %) and syngas (35 %), whereas fast pyrolysis produces bio-oil (70%) [46]. Syngas is primarily a mixture of H_2 and CO, but it may also contain CH_4, CO_2, H_2O, and other substances. Bio-oil typically contains an aqueous phase and an organic phase, with the latter being used to generate energy. Bio-oil is made up of a wide variety of compounds, the most common of which are sugars, acids, ketones, phenols, and furans [47].

2.5.3. Hydrothermal Treatment

Hydrothermal carbonization is a thermochemical process at which biomass feedstock is heated with water at a temperature range of 180 ^{o}C to 250 ^{o}C at pressurized conditions to convert to carbonaceous solid product called hydrochar and a liquid fraction [48]. Also known as coalification, hydrothermal carbonization has emerged as an efficient technology for dealing with high moisture organic waste, as it requires water for the reactions [49], [50]. Water in its sub-critical state acts as a reactant, aiding the conversion process [49]. During HTC, an organic matter goes through series of reactions, namely hydrolysis, condensation, polymerization etc. to finally attain a phenolic hydrophobic chemically stable form of hydrochar. Two other main phases are obtained after HTC, the liquid effluent and gas, are also valuable from commercial standpoint. The liquid content contains a significant number of organic compounds such as lactic acids, formic acid, furfural, acetol etc. The gas consists of mainly common greenhouse gases such CO_2, CH_4, H_2 and vapor [49], [50].

2.6.Integration of Anaerobic Digestion with Hydrothermal Carbonization

One of the main advantages of HTC over other thermochemical treatment methods is its ability to handle high-moisture waste. The digestate from anaerobic digestion, which contains over 70% moisture content and has a high volume, thus pose as a potential waste stream suitable for treatment via HTC [51]. Unlike raw waste such as municipal waste or food waste, digestate has low amount of carbon as a significant portion of the feed carbon converted to biogas [52]. The main issue with handling of digestate is its unstable form, which makes it difficult to apply as a soil amendment product. Hydrothermally carbonizing digestate slurry works as a stabilization treatment, converting it to an aromatic hydrocarbon. Hence, HTC coupled with AD-whether from downstream integration or synergistic coupling can be beneficial in upgrading the AD as a technology [53], [54]. In Figure 3, an AD-HTC coupled system is

depicted, showing how the products from both processes can be utilized as feed and facilitate a circular system. In the following sub-sections, prospects of several ways of AD-HTC integration are delved into.

2.7.Potential for Nutrient Recovery

Digestate is a nutrient-rich biogenic residue, retaining the micro and macro nutrients present in substrate for AD. Upon hydrothermal carbonization, a speciation of nutrients and heavy metals to both the hydrochar and process water have been reported in several literature [37], [55]. This distribution depends largely on feed type and operating conditions during HTC. Operating conditions such as reaction temperature, biomass to water ratio, retention time affect the final distribution of all the components in the digestate slurry into the hydrochar and process water [53], [56]. Several studies reported that hydrochar usually retains majority of the phosphorus and heavy metal of the feed [23], [30], [57]. Nitrogen and sulfur content however distributes the process water, with one study reporting that around 70-90% nitrogen distributes to the process water [57], [58]. Nutrient recovery from the process water has been gaining attention in context of recovering diminishing resources such as phosphorous. The speciation of P can be diverted towards process water by inducing acidic conditions (during HTC or after HTC process). The P then can be recovered in various forms. Some studies report the simultaneous extraction of P and N content in the liquid by struvite precipitation, where the nutrients convert to $NH_4.MgPO_4.6H_2O$ or struvite [23], [59]. Struvite can readily be utilized as a soil amendment product and thus aid in developing a circular system. Aragon et al. reported a yield of 0.02 kg P per ton of sewage sludge via struvite precipitation of process water from HTC [60]. The economic and environmental implications of nutrient recovery in the downstream of HTC are still unknown from commercial perspective and hence remains a future research directive.

2.8.Hydrochar as energy carrier

The digestate-derived hydrochar can be utilized as an energy source. AD as a standalone system only produces one product- biogas, which has low heating energy. By hydrothermally carbonizing digestate, the resulting hydrochar could be used as a combustion fuel and sold as an energy carrier in the market. However, it is unclear whether the digestate derived hydrochar possess enough C amount to be utilized as hydrochar fuel. Aragon et al. reported that producing hydrochar as fuel increases the net energy production by 10 times compared to only biogas [60]. The author reported an electric output of 312.0 kW-h per ton of digestate feed [60]. In few studies, approaches such as co-HTC and state-of-the-art heating techniques. Deng et al. reported a study on hydrothermally carbonizing anaerobic digestate for optimizing energy recovery [61]. Employing microwave-assisted low temperature HTC, the study reported carbon densification in hydrochar- resulting in a hydrochar containing 63.6% C. Hydrochar as a fuel from digestate thus can be a commercially lucrative pathway in future.

2.9.Environmental Effects of Digestate Management

Digestate handling has been indicated as a major hotspot in a biogas plant by various studies. The environmental effects of ill-management of digestate are often overlooked while improving the anaerobic digestion system. As digestate is nutrient rich, improper handling or usage could pose environmental and heal risks. Several studies have compared existing digestate management technologies from an environmental standpoint [62]–[64]. Duan et al. reported an improvement of overall life cycle impact of fractioning the digestate into solid and liquid compared to conventional treatment [65]. Styles et al. conducted an expanded life cycle assessment comparing baseline scenario of digestate production to upcycling of digestate to biofertilizer [66]. The study showed that digestate upcycling improves several categories such

as global warming, acidification, and eutrophication. However, while assuming worst-case scenario, digestate-to-biofertilizer increased global warming and cumulative energy demand due to new process inputs.

However, thermochemical treatments of digestate treatment such as hydrothermal carbonization and their implications have largely been unexplored in the literature. Celletti et al. studied the phytotoxicity of hydrochar synthesized from anaerobic digestate and found that hydrothermal carbonization reduced the bioavailability of nutrients and heavy metals significantly [55]. However, presence of furan compounds in HTC limits its ability to function as an effective biofertilizer, hence requiring proper pre or post treatment of digestate-derived hydrochar.

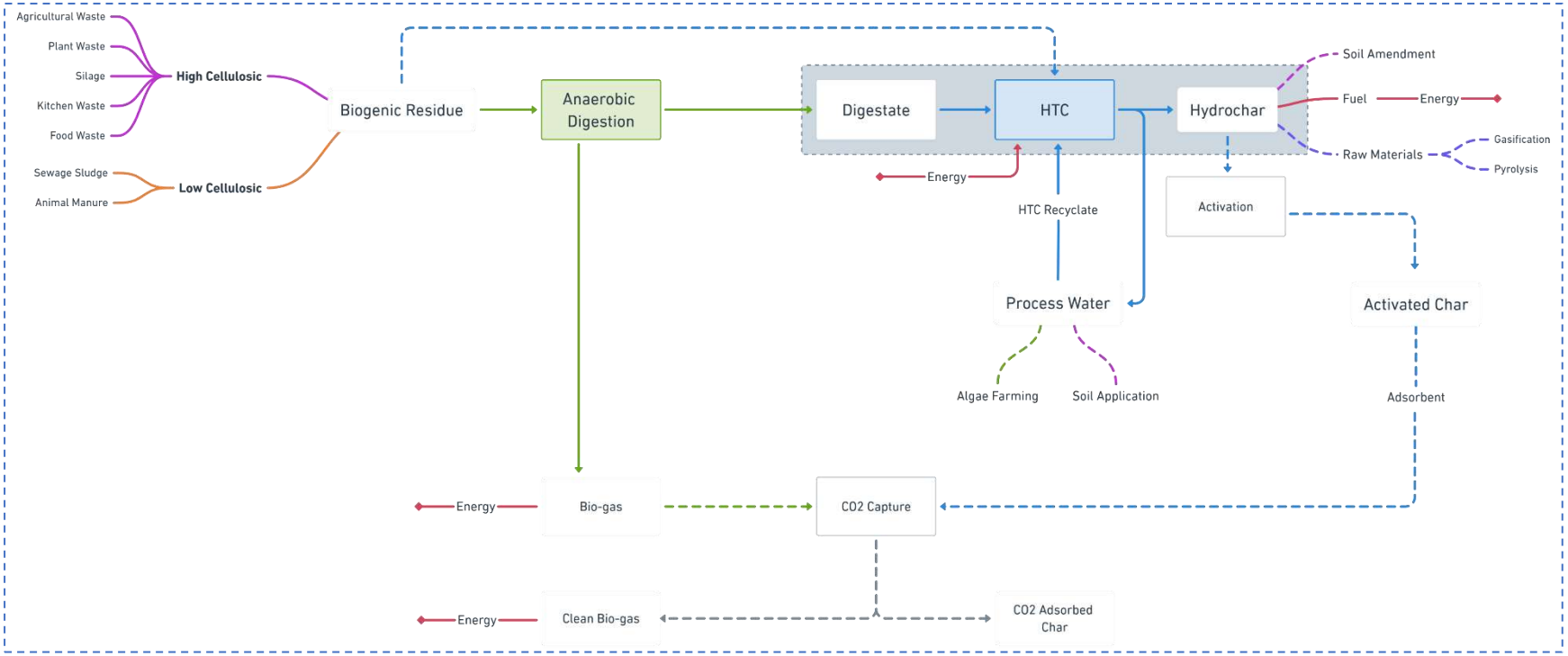


Figure 2. Integrated biorefinery concept of an AD-HTC system for waste management

Chapter 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1.Experimental Characterization

The determination of digestate-derived hydrochar is an important part of the life cycle assessment. Poultry litter digestate was collected from Samiul Agro Biogas Plant at Gazipur, Dhaka. The digestate slurry was dried at 80 ºC for 48 hours and then grinded. In Figure 2, the entire flow chart of the property analysis is explained visually. The conditions of HTC reactions have been decided via thorough literature survey.

3.1.1. Synthesis of Digestate-derived Hydrochar

The dried poultry digestate was hydrothermally carbonized in a laboratory scale autoclave reactor system (Novoclave, Büchi Glas Uster, Switzerland). At first, 10 gm of dried poultry digestate and 90 ml of distilled water were fed to the reactor vessel, thus keeping the feed to water ratio 1:9. This ratio was maintained for all reaction conditions considered. A total four reaction conditions were considered varying temperature and retention time (180 ºC, 200 ºC and 60 min, 90 min). The reactor was a 200 ml batch autoclave reactor consisting of a heating and cooling jacket, stirrer, and a bursting disk able to withhold a maximum pressure of 40 MPa. The reactor body material was stainless steel (SS 400). After loading the reactor with sample feed and water, the system was tested for leakage and purged using nitrogen. The reactor vessel required around 50 to 60 minutes to heat up to the desired reaction temperature. As the reaction completes the reactor vessel was cooled down to room temperature and the hydrochar slurry was collected in a beaker.

The slurry was then filtered using a vacuum filtration unit. Around 200 ml to 300 ml distilled water was used for washing the reaction product and during filtration. Cellulose filter paper (Sartorius, 0.45 micron) was used for filtering. The liquid effluent or process water was then poured into storage bottles. The resulting hydrochar was then dried at 105 ^{o}C in an oven (Digisystem hot air oven, DSO-300D) and later stored in airtight containers.

3.1.2. Proximate Analysis

The proximate analysis of the feed digestate and hydrochars was done following the ASTM E 871 (moisture), ASTM D 1102 (ash) and ASTM E 872 (volatile matter). Approximately 1 gm of each sample were taken in the crucibles and appropriately weighted. The volatile matter and ash content was determined following the standards and using a muffle furnace.

3.1.3. Elemental Analysis

Elemental or ultimate analysis was conducted for the samples in an Elemental Analyzer (EA 3100, Eurovector, Italy). The C, H, S and N contents were determined. Prior to the analysis, the samples were dried at 105oC for 24 hours and properly grinded for homogeneity. In the analyzer, around 0.5 to 1 mg pf samples were taken in tin capsules and loaded into the analyzer. Each test was repeated once.

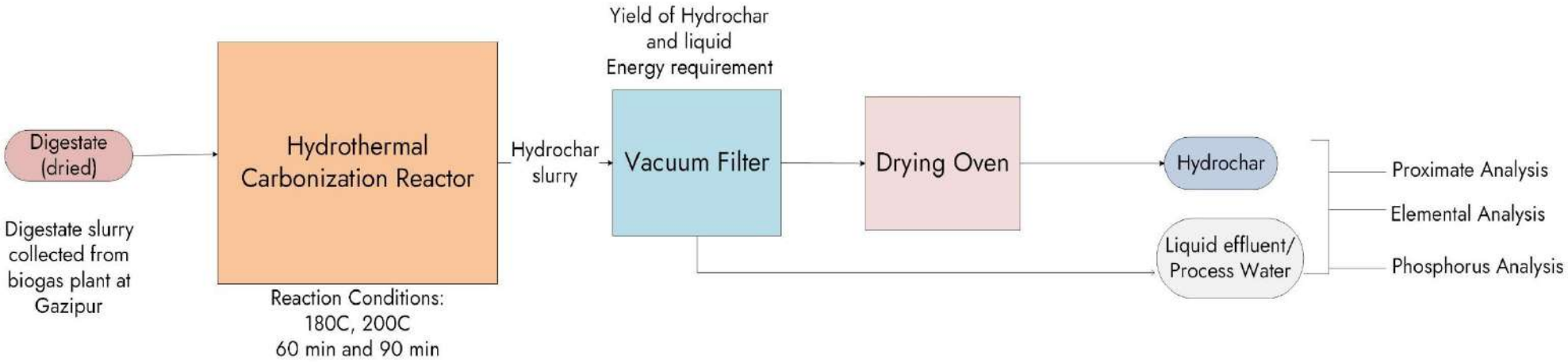


Figure 3. Experimental flow diagram for characterizing hydrochar and liquid effluent for life cycle inventory analysis

3.1.4. Determination of Phosphorous

The digestate and hydrochars were ashed at 650 ^{o}C for 2 hours. The ash of the samples were then digested for determining the P content following ASTM C 114 standard. The product liquid after digestion were analyzed with UV/Vis spectrophotometer (Hach DR6000) using PhosVer 3 phosphate reagent powder pillows. During analysis, the samples were diluted with distilled water. A wavelength of 880 nm was used for the spectrophotometer.

3.2.Life Cycle Assessment

Life cycle assessment was conducted to assess the environmental implications of an AD-HTC integrated system as compared to a standalone AD system. In this section, each step of life cycle assessment is described in detail below.

3.3.Goal and Scope Definition

3.3.1. Goal Definition and Functional Unit

The main goal of the study is to determine and compare the environmental impacts of handling in a standalone AD system and AD integrated with HTC system for the treatment of biogenic residue such as digestate. At first, the life cycle impact assessment of anaerobic digestion technologies- namely mono-digestion and co-digestion was conducted to determine how AD as a standalone technology performs and the potential hotspots of the system. Finally, hydrothermal carbonization coupled with AD (AD-HTC) was considered. The results of these two systems were then compared and analyzed.

For the life cycle assessment of AD systems (AMoD and ACoD), the functional unit or basis of 1 MJ of biogas energy produced was considered, as the two AD technologies were also compared. For AD-HTC system, 1 ton of digestate slurry from the anaerobic digester was considered the functional unit. For final comparison of the two systems, the functional unit of 1 ton of digestate slurry was considered. The choice of functional unit mainly depends on the purpose of the life cycle assessment. For the life cycle assessment of AD technologies, we considered mainly two types of agricultural residues: poultry litter, cow manure and food waste as the co-feed during co-digestion. However, for AD-HTC system, only poultry digestate was considered the representative feed.

3.3.2. System Boundary

For LCA of AD systems, we consider a cradle-to-gate system where livestock manure such as cattle manure or poultry litter was being anaerobically digested in a farm-scale biogas plant for producing biogas and digestate slurry. A medium sized farm-scale biogas plant was the main system, which is depicted in Figure 4. Livestock waste from the farm is used as the plant's primary input substrate. The system is completed by producing biogas for energy use and storing digester sludge (also known as digestate) in open caverns. Before being disposed of, a large portion of digestate is stored in open storage systems such as caverns for an indefinite period of time. Digestate is not properly commercialized as a product in Bangladesh due to legislation prohibiting the use of liquid sludge as fertilizer, with only a small percentage sold as organic fertilizer at a low selling price. As a result, digestate has been designated as a waste stream. The research spans the typical plant lifespan of 20 years. Mainly biogas production and digestate open storage were considered the main two processes.

Similarly for AD-HTC system, we consider a cradle-to-gate system, which expands to the hydrothermal carbonization of digestate slurry. The production of biogas is like the previously stated system boundary for AD technology. As HTC is an endothermic process, it required heat. We considered that the biogas from the digester is utilized partially to heat up the reactor system. For cooling of the reactor, we consider nearby underground water source. After HTC, the hydrochar slurry is filtered in a filter press system. The hydrochar is then dried and marketed as a product. As it is an attributional study, the effects of hydrochar in the market is being ignored. The liquid effluent or process water is being considered a waste-water stream and disposed to the environment. The biogas and hydrocahr are the two products for this system. Figure 5 depicted the system boundary.

3.4.Considered Cases

For life cycle assessment of AD system, we consider mainly two cases- anaerobic mono-digestion and anaerobic co-digestion. Two livestock waste such as cattle manure and poultry manure are considered. For co-digestion, food waste is chosen as the co-substrate for each of the manure. We also consider two inventory cases; in one case the life cycle inventory was calculated using experimental data derived from literature and another case explored model equations for determining the biogas yield (Table 3).

For AD-HTC system, we only consider two cases- AD and AD-HTC. Poultry manure was considered the main substrate to the digester. In both cases, we utilize both literature data and experimentally evaluated analysis.

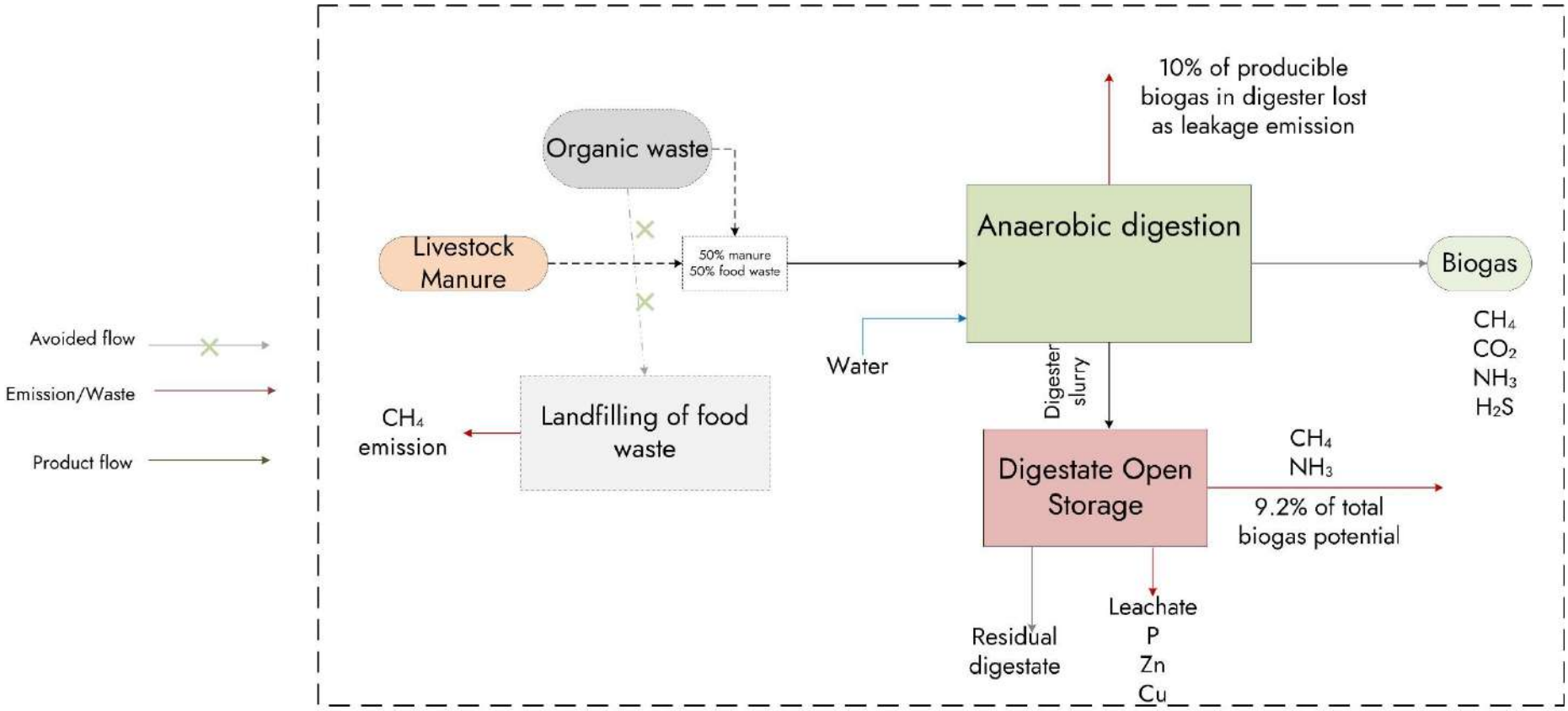


Figure 4. System boundary considered for life cycle assessment of anaerobic digestion technologies (AMoD and ACoD)

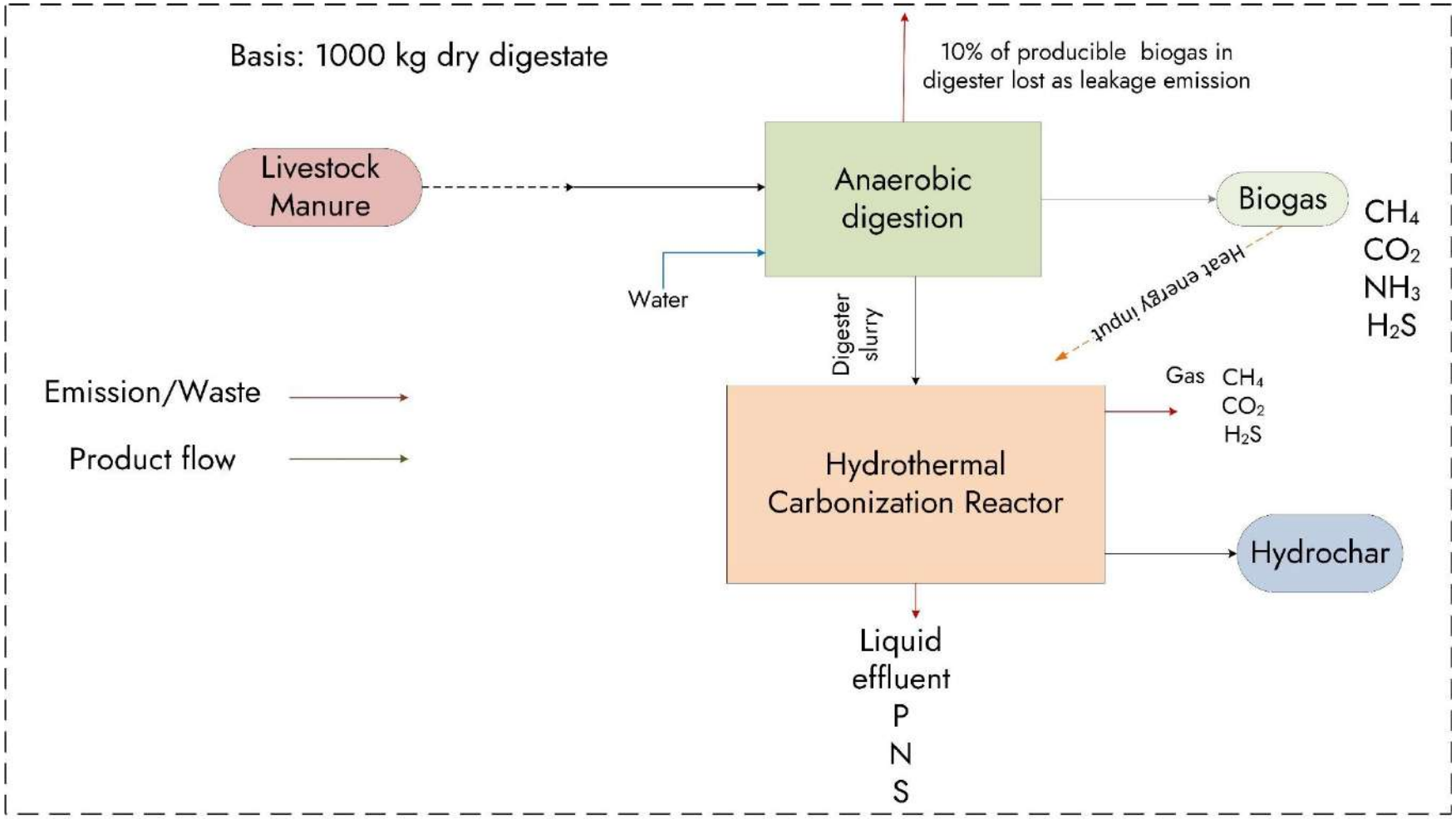


Figure 5. System boundary considered for life cycle assessment of AD-HTC integrated system

Table 3. Scenarios considered for the life cycle assessment of AD standalone system

Case/Inventory	Scenario	Name	Feed ratio
LCI-M	MB1	Mono-digestion of poultry manure (PM)	100% fresh layer poultry
	MB2	Co-digestion of PM with organic waste or food waste (FW)	50% fresh poultry manure mixed with 50% food waste
	MS1	Mono-digestion of cow manure (CM)	100% fresh cow manure
	MS2	Co-digestion of CM with FW	50% cow manure with food waste
LCI-E	EB1	Mono-digestion of PM	100% fresh layer poultry manure
	EB2	Co-digestion of PM and FW	50% fresh poultry manure mixed with 50% food waste
	ES1	Mono-digestion of CM	100% fresh cow manure
	ES2	Co-digestion of CM with FW	50% cow manure with food waste

3.5.Life Cycle Inventory Analysis

3.5.1. Data Collection and Generation

Life cycle inventory comprises field data, relevant literature-informed assumptions and calculations, and background data from secondary databases. The contribution of inventory data source and quality is critical towards interpreting the impact. In this analysis, the inventory for anaerobic digestion (AD) has been calculated in two ways and distinguished; theoretically (LCI-M) and using literature-reported experimental values (LCI-E). LCI-M model is based upon Buswell-Boyle equations for estimating the biogas yield and composition, hence considered to represent a mechanistic model for inventory development [67]. LCI-E model is constructed by utilizing biogas and methane potential reported in the literature, thus representing a literature-informed inventory model, with a detailed description of its construction discussed in the Appendix A.For life cycle assessment of AD-HTC system, the inventory was constructed using both literature and experimentally derived data were used. Table 4, Table 5 and Table 6 summarized the inventory used for conducting the life cycle assessments.

3.6.Life Cycle Impact Assessment: Selection of Method and Categories

The inventory was prepared using spreadsheeting software, MS Excel, and the impact modeling was done with OpenLCA 1.10.3. The selection of impact methods was based on the primary sources of emissions observed in inventory analysis. Life cycle impact assessments were computed using CML 2002 baseline method for five impact categories: climate change potential, acidification potential, eutrophication potential, terrestrial ecotoxicity, and malodorous air emissions.

Table 4. Life cycle inventory for AD-HTC system

Variable	**Description**	**Unit**
Reaction Condition	200 ^{o}C	90 min
Yield (wt%) of HTC	73.21	%
Amount of HC	700	kg
C in HC	266.18	kg
N in HC	72.46	kg
P in HC	12.66	kg
Zn in HC	0.315	kg
Cu in HC	0.026	kg
Amount of Liquid	9300	kg
N in liquid	13.97	kg
P in liquid	8.44	kg
Amount of gas	15.73	kg
CO_2	11.48	kg
CH_4	4.18	kg
H_2S	0.08	kg

Table 5. Life cycle inventory for LCI-E inventory model

Scenarios		EB1	EB2	ES1	ES2	Ref.
Parameter	Unit	PM	CM	PM+FW	CM+FW	
TS	kg	0.27404	0.13396	0.19396	0.11811	-
Sulfur distribution to biogas	% (w/w)	90% of sulfur to digestate and rest in biogas				[68]
Biogas density	kg/m3	1.15	1.15	1.15	1.15	-
Biogas yield	(NL/g VS added)	250	366	330	531	[69], [70]
CH_4	v/v	0.626	0.660	0.628	0.590	
CO_2	v/v	0.364	0.330	0.362	0.400	
NH_3	v/v	0.0066	0.0094	0.0077	0.0092	-
H_2S	v/v	0.0034	0.0006	0.0023	0.0008	-
Total biogas	kg	0.04719	0.04324	0.04695	0.05218	-
LHV	KJ/kg	19240	21000	19340	17400	-
CH_4	kg	0.02954	0.02854	0.02948	0.03079	-
CO_2	kg	0.01718	0.01427	0.01700	0.02087	-
NH_3	kg	0.00031	0.00041	0.00036	0.00048	-
H_2S	kg	0.00016	0.00002	0.00011	0.00004	-
Digestate	kg	0.22206	0.08635	0.14226	0.06064	-
Biogas leakage	%	10% of net biogas from digester				
Residual biogas production during digestate storage		9.2% of total producible biogas				[71]
CH_4	kg	0.0030	0.0029	0.0030	0.0031	-
NH_3	kg	3.17E-05	4.13E-05	3.68E-05	4.86E-05	-
Leaching of nutrients into soil		100%				-
P	kg	4.69E-03	1.12E-03	2.12E-03	7.87E-04	-
Zn	kg	6.99E-05	3.75E-05	3.05E-05	2.06E-05	-
Cu	kg	5.81E-06	1.47E-05	3.03E-06	7.32E-06	-

Table 6. Life cycle inventory for mono-digestion and co-digestion scenarios for mechanistically derived inventory model LCI-M calculated for a basis of 1 MJ biogas energy produced

Scenarios		MB1	MB2	MS1	MS2	Ref.
Parameter	Unit	PM	CM	PM+FW	CM+FW	
TS	kg/MJ	0.09045	0.09989	0.09355	0.11809	
CH_4	v/v	0.45458	0.47747	0.47117	0.48488	Equations from
CO_2	v/v	0.39469	0.46630	0.42038	0.46068	[67]
NH_3	v/v	0.14487	0.05479	0.10289	0.05124	
H_2S	v/v	0.00586	0.00144	0.00556	0.00320	
Total biogas	kg	0.06605	0.07267	0.06770	0.07042	
LHV	kJ/kg	15140	13760	14770	14200	-
CH_4	kg/MJ	0.03002	0.03470	0.03190	0.03415	-
CO_2	kg/MJ	0.02607	0.03389	0.02846	0.03244	-
NH_3	kg/MJ	0.00957	0.00398	0.00697	0.00361	-
H_2S	kg/MJ	0.00039	0.00010	0.00038	0.00023	-
Digestate	kg/MJ	0.02440	0.02722	0.02585	0.04767	-
Biogas leakage	%	10% of net biogas from digester				-
Residual biogas production during digestate storage		9.2% of total producible biogas				[71]
CH_4	kg/MJ	0.0028	0.0032	0.0029	0.0031	-
NH_3	kg/MJ	8.80E-04	3.66E-04	6.41E-04	3.32E-04	-
Leaching of nutrients into soil		100%				-
P	kg/MJ	1.55E-03	8.37E-04	1.02E-03	7.87E-04	-
Zn	kg/MJ	2.31E-05	2.80E-05	1.47E-05	2.06E-05	-
Cu	kg/MJ	1.92E-06	1.10E-05	1.46E-06	7.32E-06	-

Chapter 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1.Hydrochar Yield and Characteristics

Hydrochar produced in four different conditions were synthesized and analyzed. Highest yield of hydrochar was found for 180 ºC and 60 minutes while the lowest found to be 61.39% for 200 ºC 90 minutes. The overall yield was in the range of 61% to 76%, with the highest yield occurring for reaction temperature 180 ºC and 60 min retention time (Table 7). Similarly, the elemental composition also shows that the C content in hydrochar at 180 ºC, 60 min is also the highest. The hydrochar yield decreased from 76.34% to 61.39% when temperature was increased from 180 ºC to 200 ºC and retention time was increased from 60 min to 90 min. Hence, it could be observed that at higher temperatures and longer reaction time, the organic matter may have become soluble at aqueous phase and lowered the yield. Similar trend could be observed by Belete et al for hydrochar derived from swine manure and whey [57]. The solubilization of organic matter towards the liquid phase was attributed to higher reaction activities due decarboxylation and dehydration reaction [44]. The volatile matter content of the hydrochar confirm this, as highest volatile matter and lowest fixed carbon was found for hydrochar at 180 ºC and 60 min. As 180 ºC is usually considered the starting temperature of HTC, there is high possibility that digestate remained recalcitrant at this temperature and did not fully convert to hydrochar. High yield at lower temperature could also be explained by a higher ash content, ash remain unreacted during HTC reactions[72]. For instance, the ash content of hydrochar at 180 ºC, 60 min was found to be one of the highest (29.17%), while the ash content of hydrochar at 200 ºC, 90 min was found to be 23.95% (Table 8). This however does not explain the highest ash content of hydrochar at 200 ºC, 60 min, which may have resulted due to experimental error or lack of proper pressurization of the reactor.

Nutrients such as N and P was found to be in the range of 1.61% to 2.56% and 800 to 1200 ppm respectively. Highest nitrogen yield was found to be for 180C at 90 min whereas the lowest

was found to be for 200 C at 90 min. Nitrogen yield thus was influenced by higher temperature and high retention time. The lower nitrogen content at the hydrochar at high temperatures could be attributed to deamination reaction occurring during HTC, resulting in speciation of N towards the aqueous phase.

Table 7. Yield of HTC of poultry digestate at 180 and 200 ºC temperature at 60 and 90 min

Reaction Condition	Experiment	Weight of Sample feed (g)	Weight of dried hydrochar (g)	Yield (wt%)
180 ºC, 60 min	1	10.0225	7.3807	73.64%
	2	10.0092	7.6409	76.34%
200 ºC, 60 min	1	10.042	6.8802	68.51%
	2	10.0714	7.4555	74.03%
180 ºC, 90 min	1	10.0232	7.1523	71.36%
	2	10.0933	6.9168	68.53%
200 ºC, 90 min	1	10.0536	6.2067	61.74%
	2	10.104	6.20331	61.39%

Phosphorus content was found to be in the range of 800 ppm to 1200 ppm in the hyrochars. The highest retention of P was found to be in 180 ºC, 60 min and 200 ºC, 60 min hydrochars. This contradicts with the literature, which showed a higher yield of P at high temperature in hydrochar.

Table 8. Proximate, ultimate and Phosphorus contents of the hydrochar (reported in dry basis)

Sample Type	N%	C%	H%	S %	Ash Content	Fixed C	Volatile Matter	P content
					%	%	%	ppm
180 °C, 60 min	2.14	24.99	3.55	0	29.17	19.81	49.40	1200
200 °C, 60 min	1.88	23.02	3.56	0	33.49	15.24	50.53	1200
180 °C, 90 min	2.57	24.12	4.01	0	26.79	27.90	48.43	800
200 °C, 90 min	1.61	21.10	3.20	0	23.95	23.77	47.60	800

4.2.Life Cycle Impact Assessment of AD system

4.2.1. Climate Change

CH_4 and CO_2 emissions are accounted for in terms of climate change impact for the system. All scenarios involving the co-digestion of manure and food waste result in a net reduction in climate change (Figure 6a and 6b). When comparing mono-digestion to co-digestion of cow manure (MS2) and poultry manure (MS1) for model LCI-M, the climate change impact was reduced by 61 % and 50.4 %, respectively. The reductions for inventory generated using experimental values (LCI-E) reported in the literature were 117 % and 67.6 %, respectively, for scenarios MS1 and MS2, exhibiting similar patterns. The avoided emissions from food waste landfilling can be attributed to the overall better performance of co-digestion scenarios. Other LCA studies comparing mono-digestion vs co-digestion show similar trends [73], [74]. Pehme et al. conducted a consequential life cycle assessment comparing mono-digestion of cow manure and co-digestion with cultivated and unused grass [75]. The author discovered that co-digestion with unused grass resulted in 41 % greater GHG savings, primarily by avoiding landfill emissions. Edwards et al. found a similar trend when co-digesting sewage sludge with municipal waste, considering the carbon sequestration effect during landfilling (Edwards et al., 2017). Obtaining higher environmental credits for producing methane-rich, high-volume

biogas and avoiding the use of fossil fuels leads to greater GHG savings, according to several studies [74], [76]. As a result, avoided emissions and environmental credits have a huge net impact, and co-digestion outperforms mono-digestion in most life cycle assessments.

Both the biogas-producing unit and the digestate storage contributed nearly equally to CH_4 and CO_2 emissions. Biogas leakage accounts for 49.9 % and 53.5 % of emissions, respectively, in the experimental and mechanistic inventory models, whereas digestate open storage accounts for 46.5 % and 50.1 %. This could be traced back to the inventory assessment assumptions. The percentage of biogas lost due to leakage and residual digestate digestion is nearly identical (10 volume% leakage and 9.2 % of biogas assumed to be lost during digestate storage). As a result, the assumptions used during inventory valuation have a significant impact on the results.

4.2.2. Acidification Potential (AP)

Acidification potential is determined by equivalent SO_2 emissions of H_2S, SO_x, NO_x, and other nitrogenous gases as acid rain precursors. In this study, H_2S emissions are caused by digester leakage, while NH_3 emissions are caused by both subsystems. Unlike climate change, no environmental credits are obtained to offset the potential acidification. The LCA results show that the performance of co-digestion scenarios varies in trend for two inventory models (Figure 6c and 6d). The elemental composition of the feed is used to calculate the biogas amount, which does not account for the synergistic or antagonistic effects of co-digestion. As a result, the acidification potential for both co-digestion scenarios ES1 and ES2 was reduced.

Both co-digestion and mono-digestion scenarios increased the acidification potential of the LCI-E. As shown in Table 4, the increase in net biogas and, as a result, H_2S and NH_3 production during co-digestion is primarily to blame. The increase was three times greater when comparing cow manure co-digestion with food waste (scenario ES1) to poultry manure co-digestion (scenario ES2). NH_3 emissions increased in both co-digestion scenarios, but H_2S

emissions varied. This is due to the different feed characteristics of the manure and the increased biogas volume as a result of co-digestion. When compared to cow manure, poultry manure contains a higher concentration of sulfur and nitrogen. Co-digestion of poultry manure with food waste (ES1) resulted in lower H2S emissions due to the diluting effect. Cow manure has a higher sulfur content in the waste mix and a 50% increase in biogas volume due to co-digestion. Digesting cow manure with food waste (ES2) produced 1.7 times more H_2S emissions than scenario EB2, resulting in a greater increase in acidification potential.

Xie et al. observed a dual effect of anaerobic co-digestion, stating that both positive and negative mineral emissions can be expected [77]. Due to dilution, sulfur-rich substrate can provide better environmental performance when co-digested with a high carbon feed. However, digesting with a high protein waste can result in nutrient accumulation, which may not be environmentally sustainable despite the energetic benefits. When using a highly heterogeneous waste such as food waste, the uncertainty of the co-substrate properties is imminent in both scenarios. Despite the fact that the scope of this study concludes with biogas production, it is used in CHP plants or as cooking fuel. The subsequent valorization steps can increase AP even more by increasing SO_2 emission, which has a higher emission factor. The removal of H_2S remains the best solution for downstream improvement in both anaerobic mono- and co-digestion of livestock manure.

4.2.3. Eutrophication Potential (EP)

The term "eutrophication potential" refers to the excess potential caused by the fertilization of mineral compounds containing nitrogen and phosphorus. The main sources of EP in this study are ammonia emissions from leakage and digestate storage, as well as digestate phosphorus content. Because of phosphorus dilution, co-digestion scenarios reduced the eutrophication potential of both types of inventory models. Lower emissions were observed for inventory model LCI-E (54.5% reduction by scenario ES1 and 29.7% reduction by ES1), whereas higher

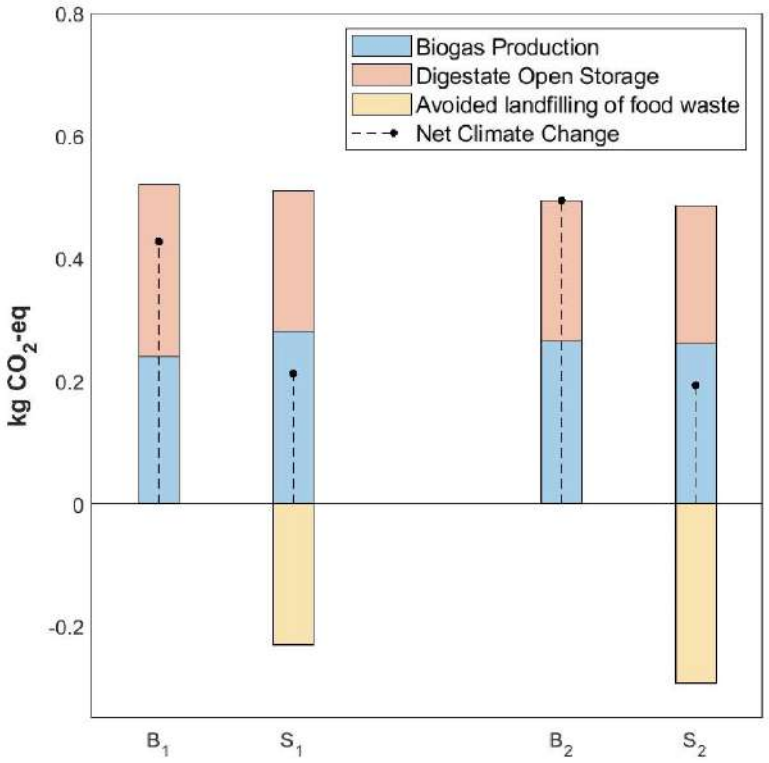
reductions were observed for inventory model LCI-E. (33 % reduction by scenario MS1 and 7% by MS2).

The findings contradict the previously reported decision, which calls for a higher EP for co-digestion. Rodriguez et al. compared co-digestion of pig manure and various types of waste to mono-digestion [78]. The majority of co-digesting scenarios increased EP, allowing for greater nutrient density. Jiang et al. discovered that co-digestion doubled EP when compared to the baseline scenario of mono-digestion [79]. Several factors can be attributed to this, including substrate characteristics, assumptions made, and avoided emission by treating digestate as fertilizer. In both studies, only ammonia is considered a major emission, whereas phosphorus in digestate is considered a fertilizer rather than an emission.

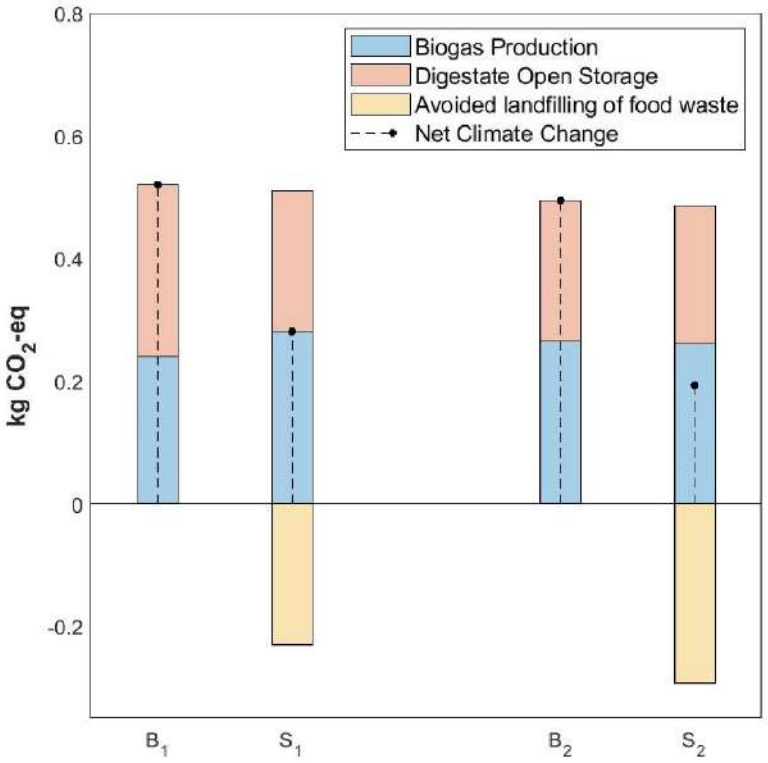
Few studies report improved co-digestion performance when mineral fertilizer emissions are avoided [75], [80]. According to Zhang et al., using digestate as organic N fertilizer increases aquatic eutrophication[80]. Pehme et al. discovered a net reduction in EP by taking into account the environmental credits of digestate as organic NPK fertilizerPehme et al. discovered a net reduction in EP by taking into account the environmental credits of digestate as organic NPK fertilizer[75]. The majority of studies, however, agree that ammonia is the most significant contributor to eutrophication, with digestate storage being the hotspot. In this study, the main contributors to eutrophication potential are still digestate open storage and land application. Both ammonia and phosphorous are considered emissions in this study. Phosphorous, on the other hand, has nearly three times the impact of ammonia.

4.2.4. Terrestrial Ecotoxicity

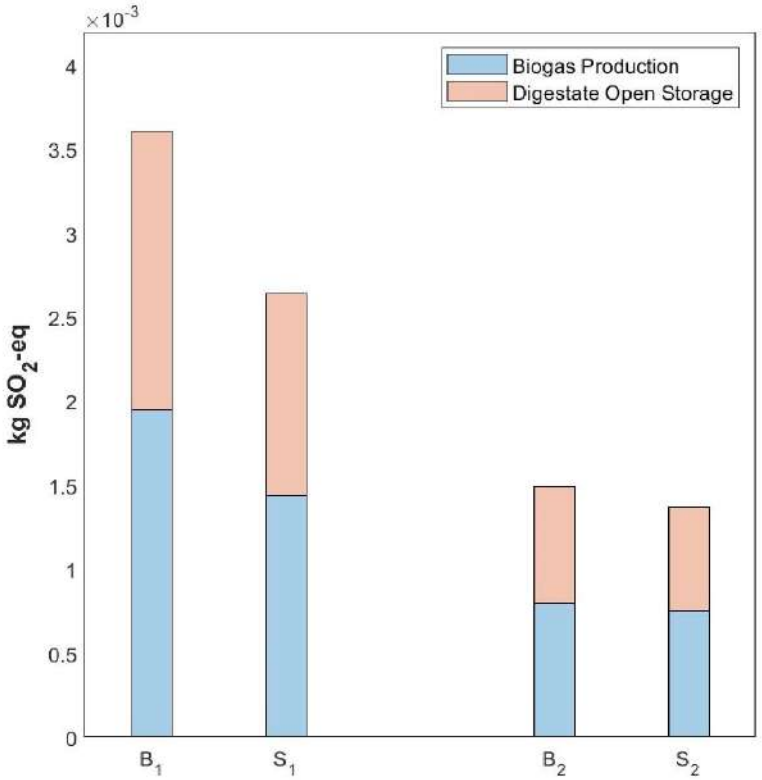
The emissions caused by hazardous heavy metal concentrations in soil are accounted for by terrestrial ecotoxicity. This impact category is primarily caused by the presence of Zn and Cu in the digestate. In co-digestion scenarios, the terrestrial ecotoxicity of mono-digestion was reduced (Figure 6g and 6h). The decrease, like EP, was caused by dilution of the heavy metal contents. When compared to mono-digestions, co-digestion of poultry manure and cow manure reduced inventory LCI-M by 35% and 28%, respectively. Because co-digestion requires less digestible solids due to higher biodegradability, co-digesting scenarios developed for LCI-E showed a higher decrease.


Biogas Production
Digestate Open Storage
Avoided landfilling of food waste
Net Climate Change
kg CO_2-eq
0.8
0.6
0.4
0.2
0
-0.2
B_1
S_1
B_2
S_2

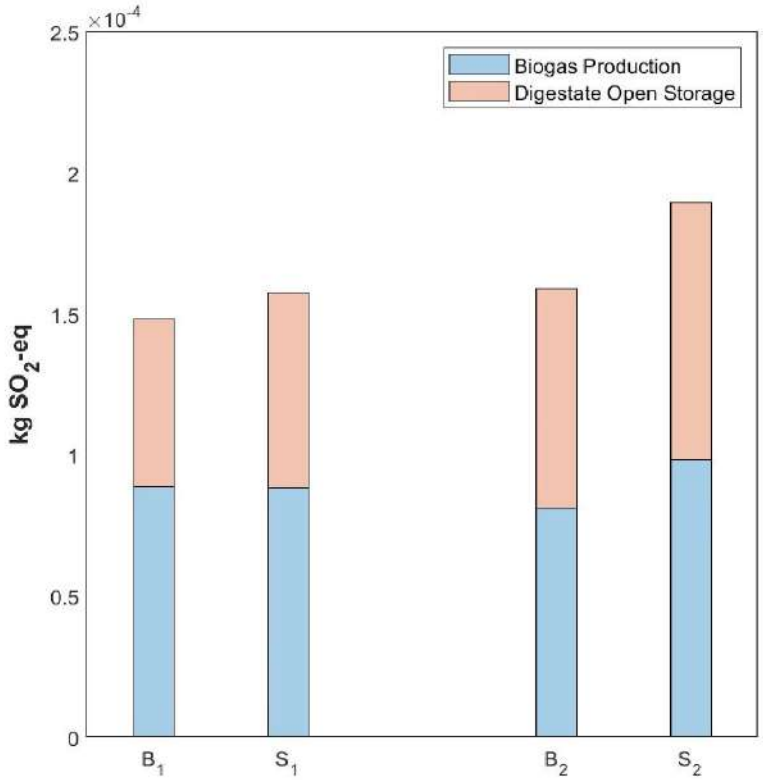
(a)


Biogas Production
Digestate Open Storage
Avoided landfilling of food waste
Net Climate Change
kg CO_2-eq
0.8
0.6
0.4
0.2
0
-0.2
B_1
S_1
B_2
S_2

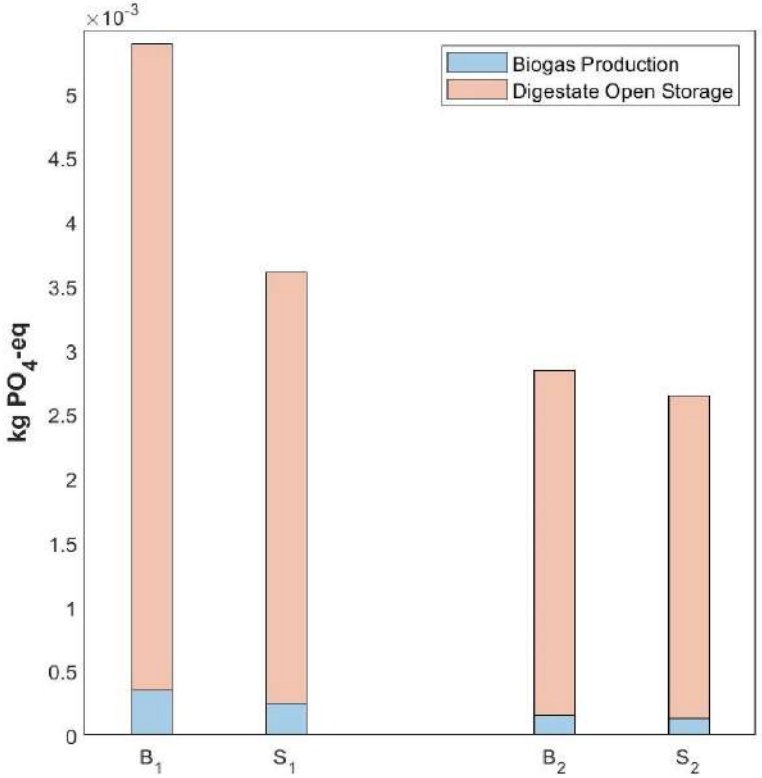
(b)


×10^-3
Biogas Production
Digestate Open Storage
kg SO2-eq
4
3.5
3
2.5
2
1.5
1
0.5
0
B1
S1
B2
S2

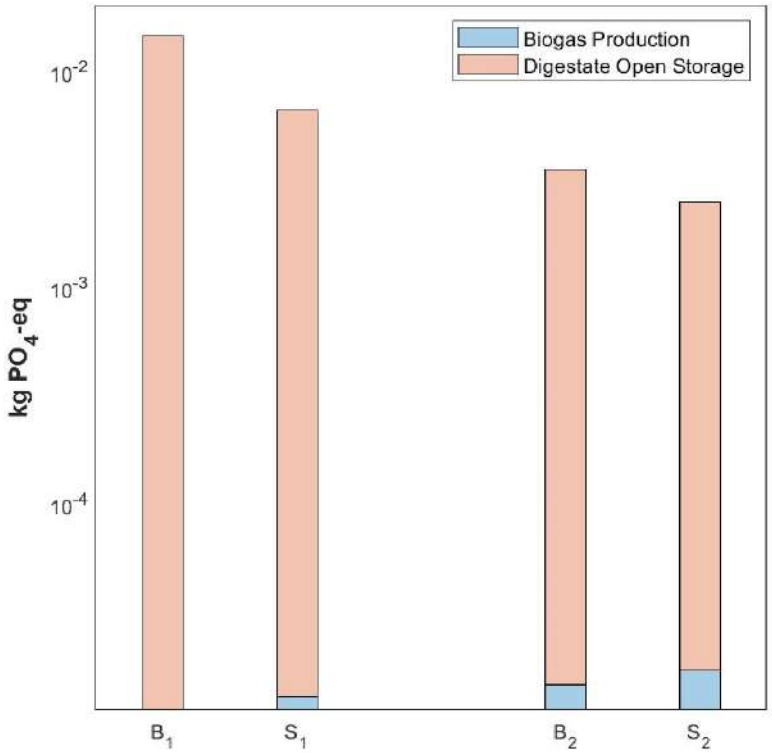
(c)


×10^-4
Biogas Production
Digestate Open Storage
kg SO2-eq
2.5
2
1.5
1
0.5
0
B1
S1
B2
S2

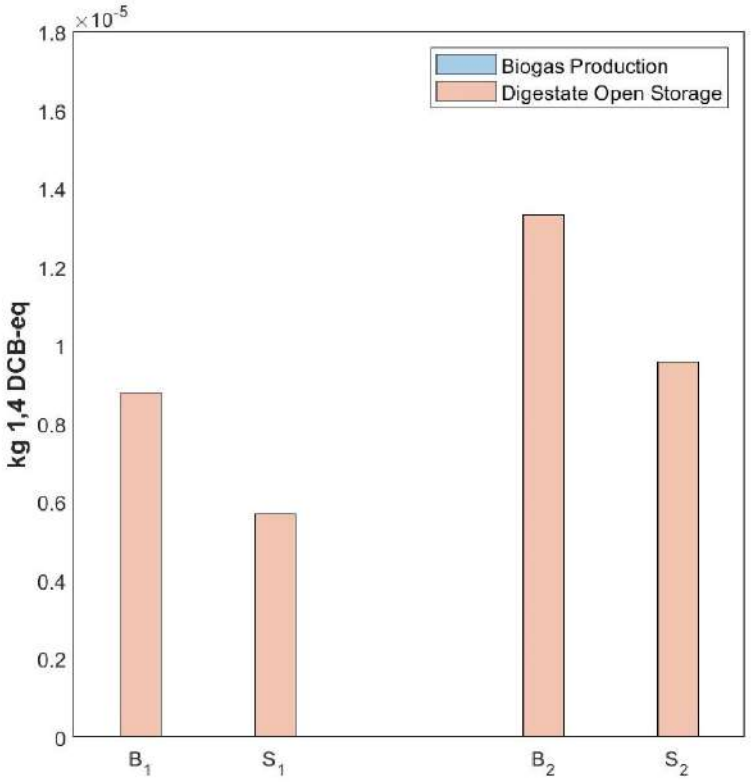
(d)


×10^-3
Biogas Production
Digestate Open Storage
kg PO4-eq
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
B1
S1
B2
S2

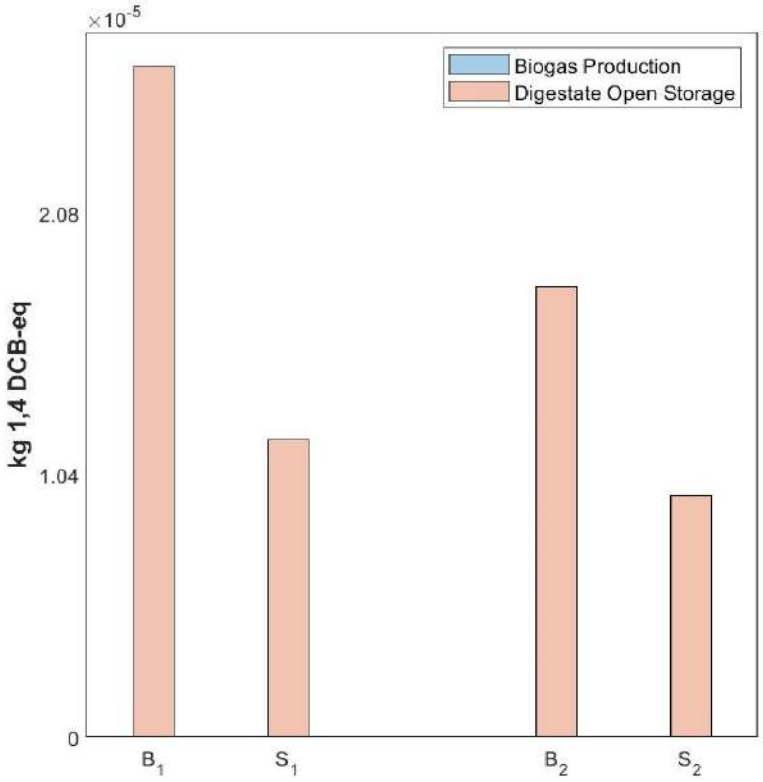
(e)


Biogas Production
Digestate Open Storage
kg PO4-eq
10^-2
10^-3
10^-4
B1
S1
B2
S2

(f)


×10^-5
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
kg 1,4 DCB-eq
Biogas Production
Digestate Open Storage
B1
S1
B2
S2

(g)


×10^-5
2.08
1.04
0
kg 1,4 DCB-eq
Biogas Production
Digestate Open Storage
B1
S1
B2
S2

(h)

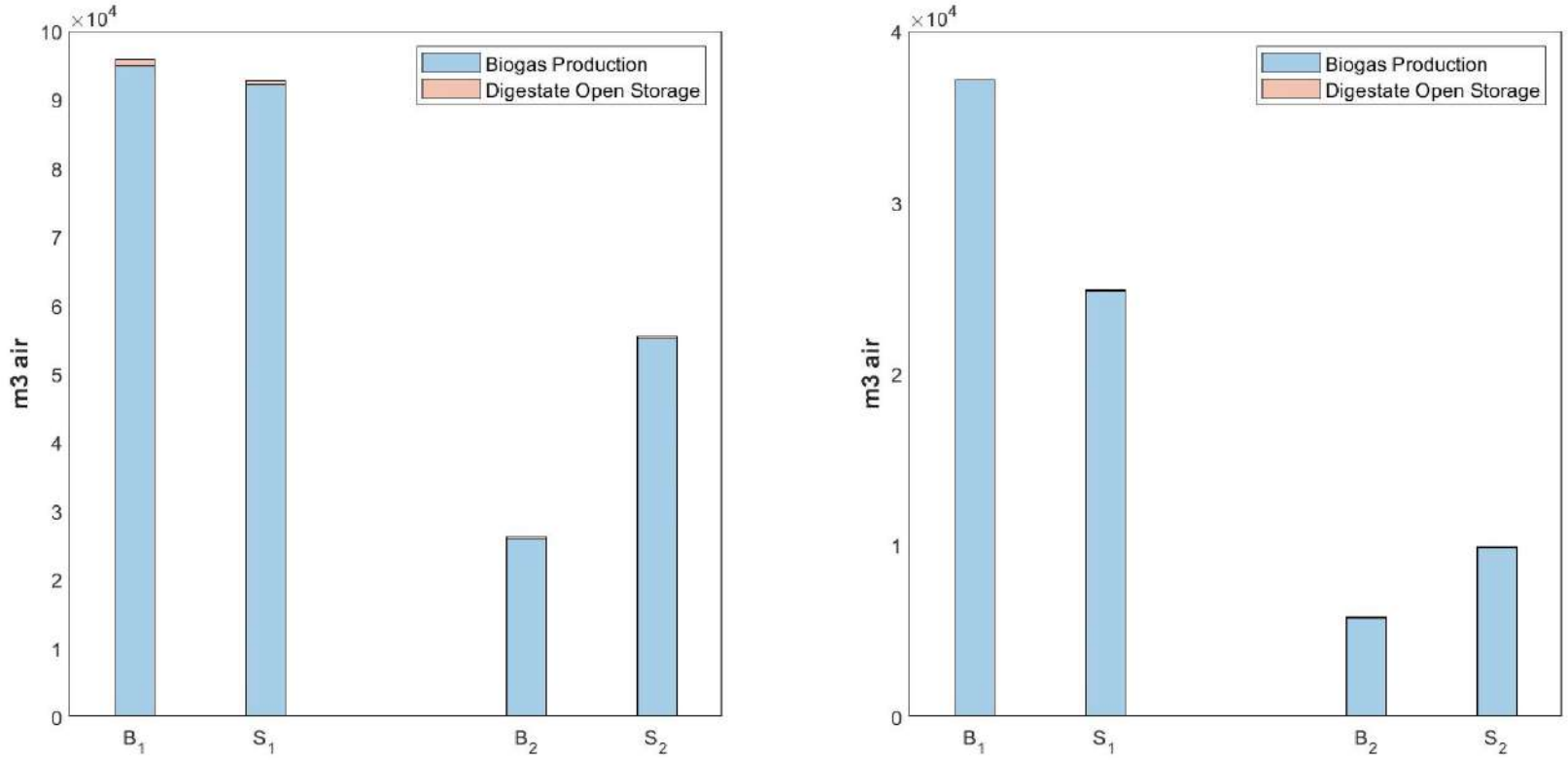


Figure 6. LCA impacts for mono-digestion (B_1, B_2) and co-digestion (S_1, S_2) scenarios. Climate change impacts for considered scenarios - (a) $LCI\text{-}_M$ (Mechanistically calculated inventory) (b) $LCI\text{-}_E$(Literature-informed inventory; Acidification potential for (c) $LCI\text{-}_M$ (Mechanistically calculated inventory), and (d) $LCI\text{-}_E$ (Literature-informed inventory); Eutrophication potential for (e) $LCI\text{-}_M$ (Mechanistically calculated inventory), and (f)

LCI_{-E} (Literature-informed inventory); Terrestrial ecotoxicity for (g) LCI_{-M} (Mechanistically calculated inventory), and (h) LCI_{-E} (Literature-informed inventory); Malodor emissions for (i) LCI_{-M} (Mechanistically calculated inventory), and (j) LCI_{-E} (Literature-informed inventory

4.2.5. Malodorous Air

Odor emission can cause major nuisance for anaerobic digestion systems. The ammonia and hydrogen sulfide released from digester leakage and digestate storage are primary causes. Because of the higher sulfur content in the feed, co-digestion scenarios involving cow manure increased malodourous emissions by 70.6 % and 111 % for inventory models LCI_{-E} and LCI_{-M}, respectively (Figure 6i and 6j). However, co-digestion of poultry manure with food waste reduced emissions for both inventories (33.1 % and 3 % for LCI_{-E} and LCI_{-M}, respectively) due to lower sulfur and nitrogen concentrations in the waste mix.

4.3.Relative contribution of subsystems

Biogas production and digestate emission had nearly equal contributions to climate change and acidification potential. For emissions calculating the effect of nutrients, such as eutrophication potential and terrestrial ecotoxicity, digestate open storage show a major contribution. Digestate open storage thus has the highest environmental impact in this study. Several other LCA findings reach similar conclusions, with digestate management being a critical source of emission for both mono-digestion and co-digestion scenarios. Controlling ammonia emission from digestate has been suggested as a means of decreasing the impact. Employing a closed storage system has been shown to significantly decrease immediate GHG emissions from digestate. The utilization of digestate as fertilizer has been identified as a long-term solution in various studies. However, the fertilization potential of digestate as compared with mineral fertilizer is debatable. Moreover, regulations regarding digestate application vary regionally, with many countries prohibiting the application of slurry digestate due to antagonistic effect on soil. Physical treatments and thermochemical modification of digestate are emerging as alternatives with both advantages and disadvantages. Future studies are necessary to assess the

life cycle impact of different digestate management technologies for improving the environmental performances of biogas plants.

4.4.Life Cycle Impact Assessment of AD-HTC system

4.4.1. Climate Change

AD-HTC system reduced the environmental impacts of most categories compared to AD system. For instance, climate change was reduced by 32% by AD-HTC system (510.52 kg CO_2 eq) compared to AD system (757.63 kg CO_2 eq) (Figure 7a). This reduction can be traced back to the hotspot found during the life cycle assessment of anaerobic digestion technologies-open storage of digestate. As the digestate slurry was converted to hydrochar, the residual GHG emissions from openly storing could be completely avoided. However, AD-HTC system still emits a considerable amount of greenhouse gas such as CO_2, CH_4, NO_x- which resulted in a significant climate change potential. The sources of these emissions are from effluent gas emission from the HTC reactor and biogas combustion for providing input heat energy for HTC reactor. Hence, the externally required energy for the HTC reactor unit mainly caused the emissions of greenhouse gas. Similar results could be found in the literature which also explored the role of HTC integration with AD or compared it with other competing technologies. Martos et al. conducted a technoeconomic and life cycle assessment for sewage sludge treatment comparing AD integrated with HTC system compared to standalone AD treatment [81]. The integration was found to reduce the net environmental impact of the system as the unconverted organic matter is captured in the hydrochar. Similar results are also observed by Benavente et al, who evaluated anaerobic digestion, hydrothermal carbonization, composting and incineration for the treatment of olive mill waste[64]. However, the author

noted in the expanded life cycle assessment that a significant amount of C content is lost during HTC, thus the energy offset value for HTC is lower than incineration. Moreover, the required energy for HTC contributed to the emissions. Mayer et al. also put emphasis on this, suggesting that the energy integration for HTC should be improved [82]. Thus, employing renewable energy or low carbon energy source for heating the reactor system and efficient management of HTC effluent gas could further improve the climate change footprint of the system.

4.4.2. Acidification

Acidification potential was also reduced by 32.2% by AD-HTC system (0.307 kg SO_2 eq) compared AD system (0.453 kg SO_2 eq). Similar to climate change, the abating the release of residual gas from digestate caused the reductions. From the inventory analysis of AD technologies (Appendix A), it was observed that around 90 (wt%) of S in the poultry litter distributes to the poultry digestate while only 10% of it goes to biogas. Around 0.09 kg H_2S per ton of digestate is emitted during the storage, which increases acidification potential. By converting digestate to hydrochar, the remaining S content is trapped into the char and liquid. However, AP caused from the digester due to leakage is still unavoidable and thus require proper H2S removal unit for biogas.

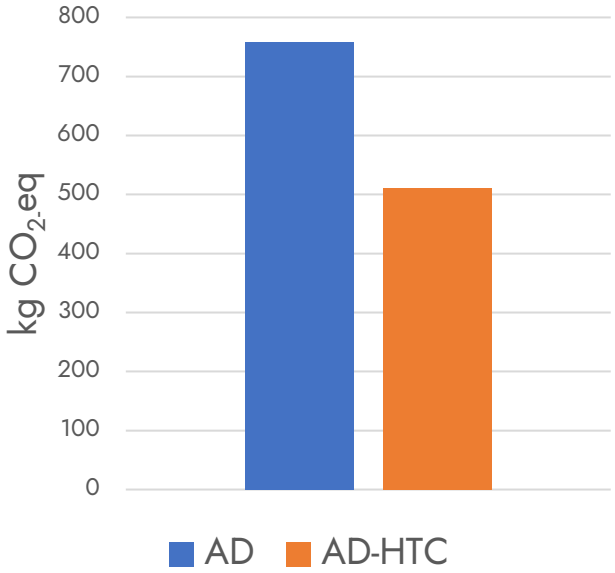
4.4.3. Eutrophication

Eutrophication potential was reduced almost 50% by AD-HTC system compared to AD. Hydrochar captured around 60% of the total P of the digestate while the rest of the 40% of P distributed to the liquid effluent [58]. The reduction of bioavailable P in liquid effluent, which is eventually disposed to the environment, resulted in lower EP. The speciation of nutrients such as P has been reported in several studies. Despite the net savings of eutrophication, the P

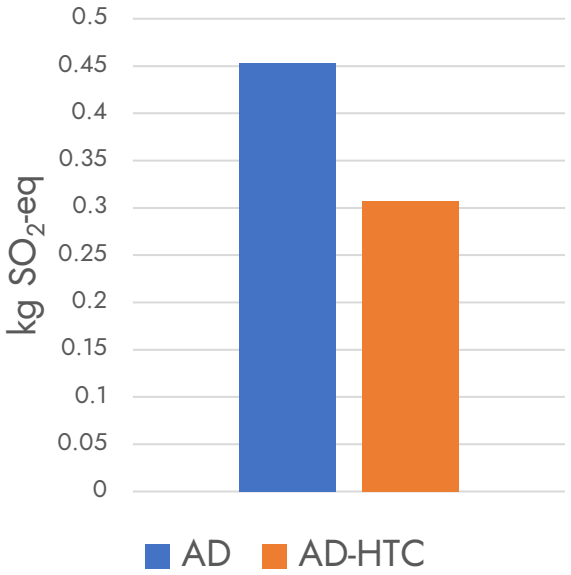
in liquid effluent still pose environmental risks. Zhang et al. determined P in process water causes notable EP and recommended the extraction of P[83]. Cui et al. reported that the P form in hydrochar and liquid depends on the HTC reaction conditions such temperature, hence future studies can conduct sensitivity analysis for different reaction conditions to optimize P recovery from the products of hydrochar.

4.4.4. Human Toxicity

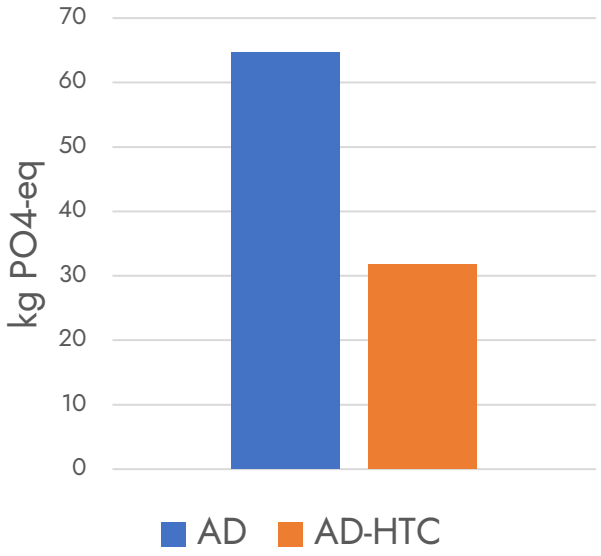
Human toxicity was reduced by 64.2% by AD-HTC system. Emissions flow of H2S and heavy metal could be traced back to human toxicity. This predominantly due to capturing heavy metal in the hydrochar. Heavy metal such as Zn and Cu were considered the main emission flows, originating by livestock agricultural activities. All of the heavy metal from the digestate distributes to the hydrochar portion.



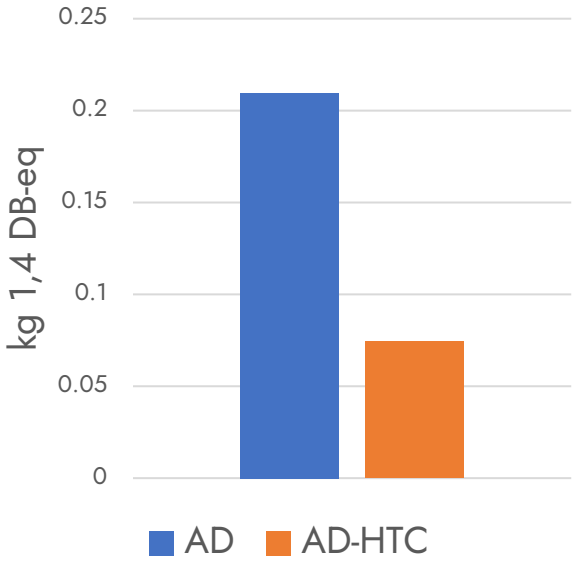
(a)



(b)



(c)



(d)

Figure 7. Life cycle impact results for AD and AD-HTC cases a) climate change, b) acidification, c) eutrophication, and d) human toxicity

4.5.Insights on improving AD-HTC system

Life cycle assessment on the considered system showed that anaerobic digestion integrated with hydrothermal carbonization reduced the net environmental impacts. However, AD-HTC system has several emission precursors which could be improved. One of the main hotspots of AD-HTC system is the process water from HTC reactor. Not only is this liquid rich in nutrients such as N and P, it also has organic contaminants such as furan compounds. The disposal of this waste stream can pose a serious threat to the environment if this technology is applied in large scale. Reuse or valorization of this waste stream is unavoidable for a sustainable outcome. As discussed in Chapter 1, process water from HTC is rich in nutrients such as P and metals. Thus, it can be a source of nutrient recovery. AD-HTC system should naturally include post treatment of this process water through which these nutrients can be recovered.

Another notable source of emissions is the energy requirement for the reactor. As hydrothermal carbonization is an endothermic process, external energy is required. To heat up the reactor, fuel needs to be burned, which would cause GHG emissions. Using biogas from AD or a fraction of digestate-derived hydrochar could be a way to integrate and optimize the heat energy requirements.

Chapter 5

CONCLUSION AND RECOMMENDATION

5. CONCLUSION AND RECOMMENDATION

5.1.Conclusion

Digestate open storage is one of the main hotspots of anaerobic digestion technologies. Life cycle assessment for anaerobic mono-digestion and co-digestion revealed that the residual CH_4, NH_3 and H_2S emitted from the open storage and biogas digester leakage cause majority of the impacts such as eutrophication, acidification and ecotoxicity. Co-digestion with food waste showed net savings and decreased three of the five impact categories such as climate change, eutrophication potential and terrestrial ecotoxicity. In context of Bangladesh, co-digestion presented an opportunity for managing multiple waste streams and thus reduce larger environmental footprint.

Experimental characterization of hydrochar from poultry digestate at different reaction conditions revealed that highest yield of hydrochar occurred at lower temperature (180 ^{o}C and 60 min), The yield was found to be decreasing and found sensitive to higher temperature, which may have increased reaction activity by increased solubilization of organic fraction. Proximate and elemental analysis reveal that hydrochar synthesized at lower temperature has highest ash content while at higher temperature and longer retention time, hydrochar has low ash content. Phosphorus and nitrogen contents were also observed to be influenced by reaction temperature, with higher temperature favoring the retention of these nutrients in the hydrochar.

Anaerobic digestion coupled with hydrothermal carbonization for the treatment of agricultural reside reduced the net environmental impacts of a standalone anaerobic digestion system, thus proving to be a better alternative integrated process. The highest reductions of about 64.2% occurred for human toxicity and 50.5% for eutrophication. These reductions can be traced back to capturing nutrients in the hydrochar, which encapsulates majority of the nutrients such P and heavy metals. Hence, the integration of hydrothermal carbonization can mitigate the

environmental disbenefits observed for anaerobic digestion technologies. However, process water from the HTC process may pose health risk if disposed to the environmental and requires mandatory post treatment.

5.2.Recommendations

This study has focused on the comparative environmental assessment of anaerobic digestion technologies with anaerobic digestion coupled with hydrothermal carbonization via attributional life cycle assessment. A few recommendations could me made based on the key findings from this study for future:

1. Co-digestion experimental data using agricultural residues found in Bangladesh should be used to properly assess the life cycle impacts of AD technologies, as the study relied on literature data and feed properties vary significantly in regions.
2. For experimental characterization, only four reaction conditions were considered. For a thorough understanding of the driving factors behind hydrochar yield and nutrient speciation in hydrochar and process water is needed. Hence, a full spectrum of operating conditions should be explored for proper experimental characterization.
3. This study is limited to evaluating the cradle to gate system of AD-HTC system. However, the end use hydrochar and process water should also be included in the future LCA studies. Expanded life cycle assessments considering nutrient recovery and potential use of hydrochar as fuel, biofertilizer or for activation should be investigated.

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APPENDIX A

The following data has been collected from a biogas plant located at Samiul Agro Farm, Gazipur, Dhaka. The biogas plant is supplied daily with the poultry litter generated from the layer farms. The system boundary of the study has been based upon the collected data.

Table A1. Collected data from Samiul Agro Poultry Biogas Plant at Gazipur, Dhaka

Category	Description
Location	Bagherbazar, Gazipur, Dhaka
Plant type	On-farm biogas plant for producing biogas from poultry manure from layer farms.
Plant scale	Medium-sized, capable of handling 1 ton of fresh poultry manure
Type of digester	Fixed dome, underground. No electrical or mechanical energy is normally used for operating the digester.
Anaerobic digestion zone	Mesophilic digestion
Downstream Operation: Biogas	The biogas generated without any cleaning, utilized in a combine heat and power (CHP) plant
Digestate management	Digester sludge stored in open caverns, fraction of it sold as fertilizer, most of it stored for a long period, spanning at least 5 years.
Odour management	No system for odour management, surrounding area is surrounded by sour smell from H2S and ammonia.
Plant lifetime	20 years
Plant maintenance	Plant maintenance occurs once or twice a year
Co-substrate availability/use	Although no co-substrates are used, the farm location is near several fruit and vegetable markets and local solid waste disposal sites within 5 km radius.

2. Feedstock Characteristics and Assumptions

2.1. Source of feedstock data

Majority of feed compositions (Volatile Solid, Ash Content, C, H, N, O contents) of poultry manure and cow manure has been taken from Quiroga et al. and Batista et al. respectively. Nutrient contents (P, Zn and Cu) of manure and food waste were taken from Bres et al. Regional data on sulfur content (0.671% and 0.194% on dry matter basis for poultry manure and cow manure respectively) of the manure was taken from a report published by IDCOL

(Infrastructure Development Company Limited), Bangladesh[84]. Properties of food waste in Bangladesh was taken from Aurnob et al., who reported the proximate and ultimate analysis of the organic fraction of municipal waste of Dhaka, Bangladesh(Kazi Aurnob et al., 2021).

Table A2. Cow manure and poultry manure properties from IDCOL

Manure	**Type of animal**	**C:N ratio**	**DM/TS**	**S% (DM)**	**N% (DM)**
Cow manure	Local cow	26-41	8% - 24%	0.004 - 0.194%	0.03 - 1.20%
Poultry Layer	Hybrid	14-17	26% - 36%	0.201 - 0.671%	1.45 - 3.95%

2.2. Biogas potential for co-digestion of manure

For inventory model LCI-$_E$, biogas potential and biomethane concentrations for mono-digestion and co-digestion of manure have been taken from literature, as reported in Table S3.

Table A3. Assumptions and considerations made for construction of life cycle inventories.

No.	Assumptions/considerations	Ref.
Logistics and Utility of the plant		
1.	No external energy for plant operation was assumed.	-
2.	Transport of food waste was assumed to be occurring in manually driven vehicles, hence no emission for transports was considered.	-
Digestate storage emission		
1.	Digestate storage emission has been assumed to 9.2% of total biogas production potential in biogas digester.	[71]
2.	No crust formation of storage was considered.	-
3.	Only CH_4 and NH_3 emission were considered, CO_2 and H_2S were assumed to be negligible/ignored.	-

4. Leaching of P, Zn and Cu was assumed 100%	-	
5. Digestate was assumed to be a waste flow, the fertilizer application was not considered. The residual digestate (mass remaining after leaching) was assumed to be stored indefinitely in the storage.	-	
Biogas leakage emission		
6. Biogas density 1.15 kg/m3 was assumed for calculation	-	
7. 10% leakage emission was considered	("CDM: Tools," 2003)	
8. For inventory calculated based on literature value (LCI_{-E}), H2S concentration was calculated considering sulfur distribution to biogas was 90% in mass basis.	[86]	

Table A4. Biogas yield and methane concentration data for LCI_{-E}

Substrate	**Mixing ratio**	**Specific Biogas Yield (SBY)**	**CH_4 in biogas**	**Ref.**
	(DM)	(NL/g VS added)	(v/v) %	
Poultry manure (PM)	-	250	62.6	[69]
PM+FW	50:50	330	62.8	[69]
Cow manure (CM)	-	366	66	[70]
CM+FW	52:48	531	59	[70]

3. Inventory Calculation

3.1. Theoretical model ($LCI_{-M)}$

Buswell-Boyle equation was used to calculate the biogas yield and compositions for mono-digestion and co-digestion scenarios [67].

The stochiometric formula for the chemical reaction for biogas formation is given by-

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right) H_20$$

$$= \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right) CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right) CO_2 + dNH_3$$

$$+ eH_2S$$

Where the constants a,b,c,d,e are mole numbers of Carbon, Hydrogen, Oxygen, Nitrogen and Sulfur respectively.

Theoretical Bio Methane Potential (TBMP)

$$= \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right)}{12.017a + 1.0079b + 15.999c + 14.0067d + 32.065e}$$

3.2. Calculations for biogas and digestate generation for LCI-M

Table A5. Calculation of biogas and digestate amount at plant scale

1625 kg total solids/day feed		Mono-digestion		Co-digestion	
Calculation		PM	CM	P+F	C+F
Stoichiometric ratio calculation (Buswell-Boyle equation)					
a	-	48.90	54.14	47.96	50.44
b	-	74.67	85.74	78.06	83.78
d	-	8.34	3.14	5.53	2.73
e	-	0.34	0.08	0.30	0.17
c	-	17.59	36.79	24.96	35.04
CH_4	mol	26.18	27.39	25.35	25.87
CO_2	mol	22.73	26.75	22.61	24.57
NH_3	mol	8.34	3.14	5.53	2.73
H_2S	mol	0.34	0.08	0.30	0.17
Total	mol	57.58	57.37	53.79	53.34
Biogas composition					
CH_4	v/v	0.45	0.48	0.47	0.48
CO_2	v/v	0.39	0.47	0.42	0.46
NH_3	v/v	0.14	0.05	0.10	0.05
H_2S	v/v	0.01	0.00	0.01	0.00
CH_4 potential	L/gVS	546.94	447.08	497.38	447.44
CO_2	L/gVS	474.88	436.62	443.76	425.11
NH_3	L/gVS	174.30	51.30	108.61	47.28
H_2S	L/gVS	7.05	1.35	5.87	2.95
Adjusted biogas amount considering 80% conversion efficiency					
Conversion efficiency %		0.80	0.80	0.80	0.80
CH_4	L/gVS	437.55	357.66	397.91	357.95
CO_2	L/gVS	379.91	349.29	355.01	340.09
NH_3	L/gVS	139.44	41.04	86.89	37.82
H_2S	L/gVS	5.64	1.08	4.69	2.36

Volume of gas at plant scale for a total solid feed of 1625 kg					
CH_4	m3	469.06	490.84	481.84	408.60
CO_2	m3	407.27	479.35	429.90	388.21
NH_3	m3	149.49	56.33	105.22	43.18
H_2S	m3	6.04	1.49	5.68	2.70
Total biogas	m3	1031.86	1028.01	1022.65	842.67
Biogas energy calculation					
Biogas density	kg/m3	1.15	1.15	1.15	1.15
Biogas mass	kg	1186.64	1182.21	1176.05	969.08
LHV	KJ/kg	15140.00	13760.00	14770.00	14200.00
Energy	MJ	17965.66	16267.15	17370.21	13760.87
CH_4	kg	539.42	564.47	554.12	469.88
CO_2	kg	468.36	551.26	494.39	446.44
NH_3	kg	171.91	64.78	121.00	49.65
H_2S	kg	6.95	1.71	6.54	3.10
Digestate amount = Total solids in feed – Produced biogas amount					
Digestate	kg	438.36	442.79	448.95	655.92

3.2. Literature-informed model (LCI_{-E})

Table A6. Calculation of biogas and digestate amount at plant scale for LCI_{-E}

Basis	1625 kg TS/day	Mono-digestion		Co-digestion	
Parameter	Unit	PM	CM	PM+FW	CM+FW
Volatile solids in the feed = VS% × Total solids in feed					
VS in feed	kg	1072.016839	1372.349439	1141.48342	1294.877708
Biogas amount = Specific biogas potential × VS in feed					
Specific biogas potential	L/g VS	250	366	330	531
Biogas Composition determination					
CH_4 (v/v) % taken from literature data					
CO_2 (v/v) % = 99% - CH4% (as 1% of biogas contains other gas components)					
H_2S (v/v) % = S% (ash free, dm) × Volatile solids in feed ×0.90×34/32					
NH_3(v/v) % = 100% - CH_4%-CO_2%-H_2S%					
CH_4	v/v	62.6	66	62.8	59
H_2S	kg in BG	1.149	0.282	1.019	0.582
NH_3	kg in BG	0.019	0.005	0.012	0.005
H_2S	L/gVS	0.845	0.208	0.749	0.428
NH_3	L/gVS	0.024	0.007	0.015	0.007
CH_4	L/gVS	156.50	241.56	207.24	313.29
CO_2	L/g VS	92.631	124.225	121.996	217.276
Total biogas potential	L/g VS	250	366	330	531
Volume % of biogas					
CH_4	v/v	62.6%	66.0%	62.8%	59.0%
CO_2	v/v	36.4%	33.0%	36.2%	40.0%
NH_3	v/v	0.662%	0.943%	0.773%	0.919%
H_2S	v/v	0.338%	0.057%	0.227%	0.081%
Total biogas	m3	268.00	502.28	376.69	687.58

Biogas density	kg/m3	1.15	1.15	1.15	1.15
Mass total	kg	308.20	577.62	433.19	790.72
Mass of biogas constituents					
CH_4	kg	192.936	381.230	272.045	466.523
CO_2	kg	112.187	190.615	156.816	316.287
NH_3	kg	2.040	5.449	3.349	7.270
H_2S	kg	1.042	0.328	0.983	0.637
Digestate production = Total solids – Biogas produced					
Digestate	kg	1316.795	1047.378	1191.807	834.283
LHV of biogas	kJ/kg	19240	21000	19340	17400
Biogas energy	MJ	5929.86	12130.06	8377.95	13758.48

4. Avoided emission due to food waste landfilling

Methane emission = Organic waste amount × DOC × DOC_f× F× (16/12 -R) × (1-OX)

Table A7. Parameters for IPCC GHG emissions per year

Parameters	**Description**	**unit**
Methane emission per year		Gg/yr
MSW(T)	total MSW generated	Gg/yr
MSW(F)	fraction of MSW disposed to solid waste disposal sites	%
MCF	methane correction factor	N/A
DOC	degradable organic carbon (fraction)	%
F	fraction of CH_4 in landfill gas	%
R	recovered CH_4	%
OX	oxidation factor	%
16/12	conversion of C to CH_4	N/A

Table A8. Values of required parameters in IPCC method

MCF	0.6	IPCC, default factor
DOC_f	0.77	IPCC, default factor
F	50%	IPCC, default factor
OX	10%	IPCC, default factor
MSW	Amount needed for co-digestion scenarios	Inventory
DOC	0.2594448	Calculated using FW data reported

Table A9. Climate change impact for diverted food waste from landfills for co-digestion scenarios.

Inventory Model	**Food waste diverted from landfill**	**Unit**	**Co-digestion Scenario**	**Climate Change Impact**	**Unit**
LCI-M	0.0468	kg	PM+FW	0.2422	kg CO2-eq
	0.0567		CM+FW	0.2935	
LCI-E	0.0970		PM+FW	0.5022	
	0.0567		CM+FW	0.2936	

4. Impact Assessment

Table A10. Impact factors considered for calculation

Impact	Flow	Category	Flow Property	Factor	Unit
Climate Change	Methane, non-fossil	Emission to air/unspecified	Mass	72	kg CO2-Eq.kg
	Carbon dioxide	Emission to air/unspecified	Mass	1	kg CO2-Eq.kg
Acidification Potential	Ammonia	Emission to air/unspecified	Mass	1.88	kg SO2-Eq/kg
	Hydrogen sulfide	Emission to air/unspecified	Mass	1.88	kg SO2-Eq/kg
Eutrophication Potential	Ammonia	Emission to air/unspecified	Mass	0.35	kg PO4-Eq/kg
	Phosphorus	Emission to air/unspecified	Mass	3.06	kg PO4-Eq/kg
Terrestrial Ecotoxicity	Copper	Emission to air/unspecified	Mass	0.14888	kg 1,4-DCB-Eq/kg
	Zinc	Emission to air/unspecified	Mass	0.17223	kg 1,4-DCB-Eq/kg
Malodor Air	Ammonia	Emission to air/unspecified	Mass	1000000.0	m3 air/kg
	Hydrogen sulfide	Emission to air/unspecified	Mass	2.3256E9	m3 air/kg