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Review

# Hydrothermal Treatment of Dairy Manure as a Pretreatment for Anaerobic Digestion: Methods, Viewpoints, and Obstacles

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## Abstract

Effective management of dairy manure is crucial for reducing environmental and public health risks. This waste material can serve as a viable source of bioenergy via anaerobic digestion. The recalcitrance of lignocellulosic fiber in manure presents challenges for its efficient conversion to methane. Hydrothermal pretreatment of manure fiber improves process performance by deconstructing the lignocellulosic structure. Low-temperature hydrothermal treatment of biomass optimally enhances the AD process performance by limiting the formation of inhibitory compounds such as furfurals. The integration of an optimal hydrothermal pretreatment within an anaerobic digestion system can improve the homogeneity, miscibility, and digestibility of dairy manure, thereby enhancing biogas yield. This review examines the hydrothermal treatment of lignocellulosic biomass, with a focus on dairy manure, the water chemistry involved in pretreatment, relevant process parameters, and the challenges faced in anaerobic digestion.

**Keywords:** hydrothermal pretreatment; anaerobic digestion; process performance; water chemistry

## 1. Introduction

The growing global demand for energy sources has sparked significant interest in renewable energy (Callegari et al., 2025; Damartzis et al., 2011; Isikgor and Becer, 2015). Bioenergy mainly comes from lignocellulosic biomass, such as wood, forestry residues, marine products, animal manure, and wastewater sludge (Ahmed et al., 2019; Mainali et al., 2023; Tursi et al., 2019; Vallejos et al., 2017). Animal waste holds considerable potential as a feedstock for this purpose. The dairy industry in the United States generates approximately 19 million tons of waste annually (Posmanik et al., 2018; Mainali et al., 2024a). Directly applying large amounts of manure from concentrated animal feeding operations (CAFOs) raises social and environmental concerns. Excessive manure application to soil can cause nutrient leaching into groundwater or runoff that leads to eutrophication (Mainali et al., 2024b; Mainali et al., 2025). It is crucial to address the spread of potential pathogens associated with manure waste. Converting animal manure into bioenergy through anaerobic digestion offers an effective method for transformation and waste management, thereby lessening ecological impacts (Font-Palma, 2019; Kumar et al., 2018; Mainali et al., 2024) and supporting energy security along with positive socioeconomic benefits. Historically, producing alternative fuels and value-added chemicals from waste biomass has relied primarily on two conversion pathways: thermochemical and biochemical methods. Biochemical processes are mostly well-developed and widely employed, as documented in current literature (Amin et al., 2017; Xu, Ning, et al., 2019). However, these methods

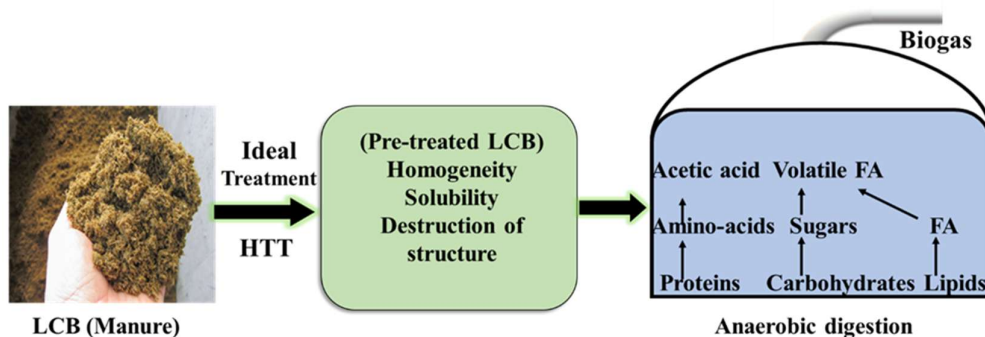
alone are not efficient for treating lignin-rich organic waste, such as dairy manure. Conventional thermochemical technologies like pyrolysis and gasification are not suitable for processing biomasses with high moisture content, including dairy manure (Gollakota et al., 2018; Nazari, L., 2016; Brown R, 2019; Mehrez et al., 2025). Conversely, various types of solid and liquid biomass waste—including high-organic-content wastewater, animal manure, and agricultural residues—can produce biogas through anaerobic systems.

Anaerobic digestion (AD) is an established technology that converts the organic part of waste biomass into sustainable fuel, specifically methane, in the absence of oxygen (Park et al., 2020; Rasapoor et al., 2020; Atelge et al., 2020). It can (AD) serve as an effective treatment method of wastes from animal agriculture, offering advantages across various concerns (Callegari et al., 2025; Razavi et al., 2019). The primary benefit of anaerobic digestion of dairy manure is the mitigation of uncontrolled methane emissions and their detrimental impact on greenhouse gases. AD provides notable advantages for dairy farms, such as odor management, waste stabilization, insect management, pathogen reduction, nutrient conservation, and mineralization. Numerous studies have documented the conversion of manure waste into renewable energy, specifically methane gas through anaerobic digestion (Gyadi et al., 2024; Tufaner and Yasar, 2016). Dairy cow manure is a readily accessible resource employed in anaerobic digestion. AD is executed through sequential and separate phases: Hydrolysis, Acidogenesis, Acetogenesis, and Methanogenesis (Meegoda et al., 2018; Ahmed et al., 2019; Zhang et al., 2012). Biogas production from manure wastes is constrained by factors including challenging degradability, a low C/N ratio, and minimal volatile solids (VS) (Szogi et al., 2015; Park et al., 2020). The slow and partial degradability of manure constitutes the primary limitation of the conventional anaerobic digestion process.

A drawback is that anaerobic microbes can convert only a specific proportion of organic mass into CH<sub>4</sub> during digestion. A substantial amount of carbon still stays in the digestate in the forms of cellulose, hemicellulose, lignin, and proteins (Park et al., 2020; Khalid et al., 2011; Kunz et al., 2009). Research studies have indicated that hydrolysis is the foremost rate-limiting step (Ahmed et al., 2019; Atandi and Rahman, 2012). Diverse feedstock types can be utilized in the anaerobic digestion process to produce fuel and value-added products (Li et al., 2010; Xu et al., 2018; Senol et al., 2020; Chen et al., 2020). Biogas composition depends entirely on the substrate used and digestion conditions (Cantero-Tubilla et al., 2018; Rasapoor et al., 2020). Biogas mostly comprises methane and carbon dioxide, along with trace quantities of other gases like nitrogen, hydrogen, hydrogen sulfide, ammonia, and water vapor.

Prior research on pretreatment for AD mostly concentrated on the hydrothermal treatment of various lignocellulosic biomass, including algal biomass, sewage sludge, and food waste inside the biorefinery process (Kumar A and Sharma S., 2017; Ahmed et al., 2018; Ruiz et al., 2013; Tekin et al., 2014). However, process inhibition is commonly noticed during digestion (Uludag-Demirer et al., 2008; Paudel et al., 2017; Neshat et al., 2017). Animal dung consists of lignocellulosic fibers that remain undigested by the animals. Dairy cow excrement contains approximately 40-50% fibrous lignocellulosic material, primarily derived from plant sources, that remains undigested in bovine rumen (McVoitte and Clark., 2019). The resistant nature of manure fiber hinders the rapid access of microbes to the feedstock (Liao et al., 2006 Together with proteins and extractives, lignocellulosic biomass (LCB) is mostly made up of three polymers: cellulose, hemicellulose, and lignin. These polymers are arranged in intricate, non-uniform three-dimensional structures to differing degrees and with various relative compositions depending on the type of lignocellulosic biomass (Isikgor and Becer, 2015). In anaerobic environments, lignin exhibits resistance to breakdown due to intermolecular interactions and the crystallinity of cellulose fibers. It also limits the hydrolysis efficiency of cellulases. The diversity and intricacy of their structures account for their rate-limiting stages and process inhibition. Therefore, pretreatment is often needed before use in AD for biogas production (Atelge et al., 2020; Phuttaro et al., 2019). Numerous studies performed on various pretreatment techniques evaluated the advantages and disadvantages of each treatment ahead of the anaerobic digestion process (Kucharska et al., 2018; Kumar et al., 2020; Putro et al., 2016; Baruah et

al., 2018). Nevertheless, optimal hydrothermal pretreatment, particularly for wet biomass, such as dairy manure, is scarce. Figure 1 below shows the schematic integrated hydrothermal treatment of dairy manure.



**Figure 1.** Schematic of integrated hydrothermal processing of dairy manure before AD.

## 2. Hydrothermal Processing

Hydrothermal liquefaction converts biomass into liquid bio-crude (Dimitriadis and Bezerigianni, 2017; Mehrez et al., 2025). Hydrothermal processing produces a high yield of an aqueous phase, thereby enhancing the potential methane yield through anaerobic digestion (Ahmed et al., 2018; Tekin et al., 2014; Funke et al., 2010). Coupling hydrothermal processing with anaerobic digestion could be an alternative strategy to enhance overall process performance (Ahmed et al., 2018; Mukherjee et al., 2020). Most organic solid waste can be destroyed and dissolved by advanced technology in the presence of oxidizing agents (Mainali et al., 2024a; Munir et al., 2018). In this process, complex organic solid wastes are broken down into smaller molecules, including short-chain acids, bio-crude oil, carbon dioxide, and water (Awasthi et al., 2019; Zhang et al., 2010). Hydrothermal oxidation transforms heteroatomic biomass species into safe products, unlike the harmful byproducts of carbonization and combustion, such as ammonia and nitrogen oxides (NO<sub>x</sub>) (Mainali et al., 2024a). The hydrothermal process is receiving increasing attention because of the unique inherent properties of high-temperature water (Cao et al., 2017). The supercritical state of water has a high ion yield and a low dielectric constant, which are favorable for promoting chemical reactions without catalysts. HTT offers several advantages over other thermochemical technologies, including the absence of acid-base catalysts, compatibility with a wide range of bioresources, complete utilization of carbon content, and, most importantly, the production of low-oxygen-content bio-oil as the main product (Ahmed et al., 2019; Peterson et al., 2008). Given its promise for treating wet waste (dairy manure), this review aims to provide the pretreatment chemistry of hydrothermally treated waste and its potential use as a pretreatment for AD. Integrated hydrothermally processed waste in a versatile AD bio-refinery can offer a sustainable and cost-effective solution to current waste disposal problems and resource recovery from organic solid waste. Among these, co-digestion of protein- and lipid-rich waste biomass (food waste) with dairy manure is an evolving field of sustainable AD biorefinery (Neves et al., 2009; Aierzhati et al., 2019; Paudel et al., 2017).

## 3. Dairy Manure AD System: A Potential Future Energy Source

Dairy manure is a low-value energy source with significant potential for biogas (Ahmed et al., 2019; Gyadi et al., 2024; Paul and Dutta, 2018). The chemical composition and properties of manure are significantly influenced by the digestibility, protein, and fiber contents of the forage, the age of the animals, and the environment of the CAFO system (Chen et al., 2018; Surendra et al., 2015; Atandi and Rahman, 2012). CAFOs are a sustainable source of refuse biomass that generates manure year-round (Ekpo et al., 2014). The rise in the number of CAFOs has resulted in an excess of manure relative to the needs of local cropland. The misuse of manure can spread various pathogens and

organic contaminants, negatively impacting human health and the ecosystem upon environmental release (Cole et al., 2000; Font-Palme, 2019; Szogi et al., 2015). Intensified livestock production constitutes a significant source of greenhouse gas emissions (CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>). Methane emissions during manure handling and storage are particularly concerning due to their high global warming potential (Feng et al., 2018). Animal manures provide essential nutrients, particularly nitrogen (N) and phosphorus (P), which are vital for crop growth (Hagos et al., 2017; Awasthi et al., 2019). Nonetheless, these highly mobile nutrients have emerged as non-point source contributors to eutrophication in multiple aquatic systems (Kumar et al., 2018; Vikrant et al., 2018; Marshall et al., 2017; Mainali et al., 2024). To mitigate these environmental impacts, advancements in treatment and management technologies are necessary, considering both ecological protection and the economic feasibility of the processes involved (Park et al., 2019; Khalid et al., 2011; Kunz et al., 2009). Stockpiled manure provides a comfortable habitat and safe ground for the growth of various pests, ranging from insects to rodents. More importantly, anaerobic digestion addresses current issues such as odor management, water pollution, pathogen reduction, pest control, and greenhouse emission reductions (Niles et al., 2019). On average, dairy manure contains 31% cellulose, 12% hemicellulose, 12.2% lignin, 12.5% crude proteins, and 12.5% starch (Chen et al., 2018; Islam et al., 2018; Atelge et al., 2020). The carbohydrate components, specifically cellulose and hemicellulose, become fermentable following hydrolysis (Chen et al., 2003). Therefore, manure can serve as a biorefinery feedstock via anaerobic digestion. The AD system offers several important benefits without demanding cumbersome and costly maintenance procedures. These systems can be adjusted to suit the climatic conditions of any country (Atandi and Rahman, 2012; Hagos et al., 2017). A critical component of dairy manure is the recalcitrant fibrous material that survives the cow's digestion process (Elalami et al., 2019; Mukherjee et al., 2020). Research indicates that only 20-30% of the initial manure fiber is converted into methane (Liao et al., 2006). This incomplete conversion leads to a substantial volume of digests and an aqueous mixture of effluents that are suitable for agronomic applications (Pelaez-Samaniego et al., 2017). AD fiber presents numerous potential avenues for revenue enhancement, including applications in dairy bedding, soil amendments, composite materials, and liquid fuel, etc. (Ahmed et al., 2018; Pelaez-Samaniego et al., 2017). These organics require further processing to optimize their economic value (Atandi and Rahman, 2012). Consequently, pretreating manure before anaerobic digestion is an effective strategy to enhance digestion efficiency and increase biogas production (Ahmed et al., 2018; Pelaez-Samaniego et al., 2017). The table below presents representative compositions of lignocellulose in dairy manure. Dairy manure also contains various extractives, including lipids, proteins, starch, and inorganic substances. The anaerobic digestion (AD) process is intricate; however, understanding the lignocellulosic composition of manure informs suitable pretreatment methods applicable to each type.

**Table 1.** Typical lignocellulosic composition of manure.

Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Cattle manure	14.2-27.4	12.2-21.4	6.1-13	Chen et al., 2003; Liao et al., 2006
Animal				
Dairy	12.2	27.4	13.0	Chen et al., 2005
Cow	21.38	20.45	11.48	(Orlando and Borja., 2020)
Swine manure	13.2-13.9	20.4-21.9	4.1-6.4	Chen et al., 2003
Poultry manure	7.7-12.0	16.4 -21.5	4.1 -7.2	Chen et al., 2003; Liao et al., 2006
Raw dairy manure	21.7	17.2	14.5	Teater et al., 2010
Anaerobic Digester (CSTR)				
AD Fiber	33.9	15.9	21.1	Teater et al., 2011

The data in the table exhibits variation and significant dispersion. The digestibility of animals varies across different regions of the world (Li et al., 2015). Cellulose serves as the primary structural

element of cell walls, contributing to the mechanical strength and chemical stability of lignocellulosic biomass. Hemicellulose is a copolymer that is composed of a variety of C5 and C6 carbohydrates that are present in the cell wall (Amin et al., 2017; Baruah et al., 2018). After hydrolysis, the carbohydrate components (cellulose and hemicellulose) are fermentable. Nevertheless, the intrinsic attributes of lignocellulosic dairy manure, including its structural and chemical qualities, render it resistant to biodegradation by enzymes and microorganisms (Pavlovic<sup>A</sup> et al., 2013; Rasapoor et al., 2020). Lignin is an amorphous phenolic macromolecule characterized by significant variability due to the coupling of 4-hydroxyphenylpropanoids. Lignin generally serves as a significant impediment to the biochemical conversion of lignocellulosic biomass, such as dairy manure (Rafique et al., 2010; Bayat et al., 2019). The valorization of lignin-rich fractions in an anaerobic digestion process can be enhanced through effective pretreatment. A sustainable and cost-effective solution is essential for the disposal and resource recovery of organic solid waste.

#### 4. Pretreatment of Lignocellulosic Biomass

Pretreatment is the initial phase in addressing the recalcitrance of lignocellulosic material for anaerobic digestion (Baruah et al., 2018; Kucharska et al., 2018). It pertains to the disruption of lignocellulosic biomass to render cellulose and hemicellulose in the pretreated solids accessible for enzymatic hydrolysis into fermentable sugars (Xu et al., 2016; Kumar et al., 2009). The primary objective of pretreatment is to reduce size, enhance surface area, minimize inhibitor development for fermentation, and recover lignin for conversion into useful products (Brodeur et al., 2011; Karimi et al., 2016). Thermochemical methods appear to be more effective than various biological, chemical, and physical pretreatments in enhancing cellulose susceptibility to enzymatic action. The traditional pretreatment methods include direct anaerobic digestion, without any treatment, cost-intensive and chemical and energy-intensive (Zheng et al., 2012). The management of organic solid waste across various temperature ranges improves anaerobic digestibility (Atelge et al., 2020; Van et al., 2018).

Various pretreatment methods, including thermal, chemical, biological, and mechanical, have been documented in the literature before the anaerobic digestion process on primary sludge and lignocellulosic biomass, such as dairy manure (Yuan et al., 2019; Shah et al., 2020; Xu et al., 2016). Physical and mechanical pretreatment techniques are typically utilized to enhance microbial access to hydrolyzable polymers and diminish cellulose crystallinity (Sayara and Antoni., 2019). While physical and mechanical pretreatments do not generate inhibitory chemicals, they are also energy-intensive processes. Chemical pretreatment possesses multiple drawbacks, including the elevated expense of acids and alkalis, the requirement for a corrosion-resistant reactor, and the necessity of neutralization before the downstream digestion of lignocellulosic biomass. Furthermore, acid use in lignocellulosic pretreatment has been linked to the generation of inhibitory byproducts, including furfural and HMF (Ahmed et al., 2019).

Likewise, steam explosion is an energy-intensive procedure requiring a properly engineered high-pressure vessel (Baruah et al., 2018; Kumar et al., 2009). Biological pretreatment is frequently sluggish and less efficacious (Amin et al., 2017; Maurya et al., 2015). Furthermore, biological pretreatments are susceptible to fluctuations in the feedstock. Toxic chemicals can readily impede the function of microorganisms in manure (Maurya et al., 2015). There have been several research studies recently published on the thermochemical and biochemical processing of third-generation (algae fuel from a microbial community) biofuels (Paul and Dutta, 2018; Kumar et al., 2018; Cao et al., 2017; Tekin et al., 2014). Nonetheless, there remains a deficiency of research studies concerning the hydrothermal preparation of dairy manure. Due to the substantial capital expenditure associated with anaerobic digestion facilities, it is prudent to minimize any additional infrastructure and labor expenditures incurred from the separate processing of organic waste (Atandi and Rahman, 2012). Consequently, it is advantageous to utilize existing infrastructure, such as the digesters often constructed at wastewater treatment facilities or on farms for manure processing, for all potential diverse wastes (Elalami et al., 2019; Xu et al., 2018).

A bio-refinery is a comprehensive concept wherein various biomass feedstocks are transformed into a diverse array of valued products through integrated processes. Biogas can be generated from several feedstocks, including agricultural residues, animal waste, and urban organic waste. Organic waste constituents, including lipids and proteins, affect biogas and methane production. The primary obstacles associated with the anaerobic digestion system include poor methane yield, prolonged retention time requirements, and the presence of non-digestible substrate components. Consequently, certain pretreatment methods or alternative anaerobic digestion configurations are essential to mitigate the detrimental impacts of substrates, as exemplified by dairy manure (Atelge et al., 2020).

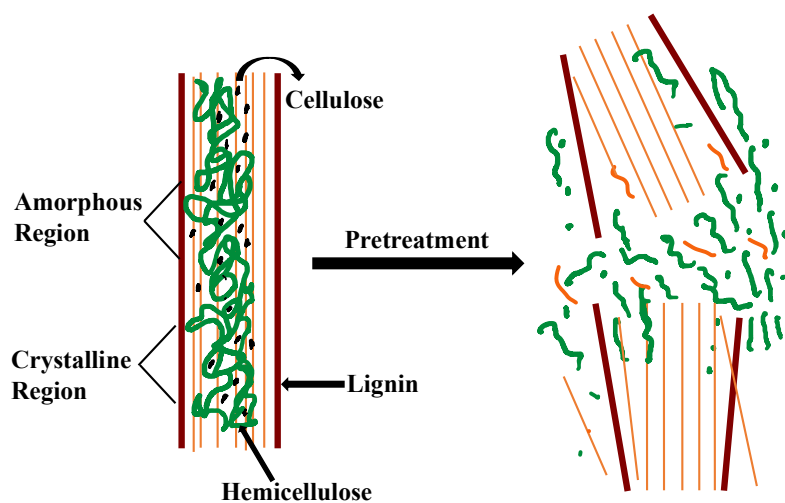
Additionally, the pretreatment technique should be commercially feasible and shouldn't slow down the processes that determine the rate, including fermentation and hydrolysis (Pelaez-Samaniego et al., 2017; Hrnčić et al., 2016). Dairy manure serves as a prevalent substrate for anaerobic digestion due to its high nutrient content. However, it exhibits low biodegradability attributed to its substantial lignocellulosic fiber content, which ranges from 40 to 50% (Chen et al., 2005). To tackle this major hindrance, suitable pretreatment techniques are required to efficiently degrade organic matter (Amani et al., 2010). The suitable pretreatment technique should enhance methane yield by disintegrating the cell walls of the substrate, solubilizing the hemicellulose and lignin effectively, so that effective microbial hydrolytic activity occurs in AD (Ismail and Tinia, 2015; Ahmed et al., 2019). Hydrothermal pretreatment represents a viable method for achieving this objective. Most research has focused on sludge and effluents, with limited studies addressing the thermal pretreatment of dairy manure (Yousefifar et al., 2017; Hii et al., 2014). This review aims to address the knowledge gap regarding hydrothermal pretreatment and its application to wet biomass, specifically dairy manure. It examines the effects of water chemistry during hydrothermal processing on structural changes post-treatment, as well as the associated process design challenges.

#### *4.1. The Steps and Reaction Paths for Hydrothermal Treatment*

Hydrothermal treatments typically denote the thermal processing of wet animal manure without prior drying. A variety of terminologies have been documented in the literature, including liquid hot water pretreatment, hot compressed water pretreatment, hydro-thermolysis, and wet torrefaction, among others (Yan et al., 2009; Zheng et al., 2014; Munir et al., 2018). Nonetheless, there exist certain subtle distinctions within each process. The hydrolysis of organic matter, followed by oxidation, through a series of chain reactions, constitutes the primary pathways of reaction (Munir et al., 2018; Yousefifar et al., 2017). Furthermore, wet air oxidation may serve as a method for the solubilization of raw materials. Moreover, this process is characterized as an oxidative hydrothermal reaction that transpires at elevated temperatures ranging from 150 to 300 °C and under pressures between 20 and 150 bar, all in the presence of oxygen (Mainali et al., 2024; Munir et al., 2018; Hii et al., 2014). During this process, thorough oxidation yields carbon dioxide and water. Nonetheless, the process of deconstructing biomass is contingent upon the specific oxidants employed and the prevailing reaction conditions (Kumar et al., 2020). In the context of oxygen delignification, the presence of oxygen enhances the reaction rate and produces free radicals under conditions of elevated temperature and pressure (Hendriks et al., 2009). The comprehensive analyses of individual hydrothermal processing methods fall outside the scope of this review. Readers should consult published articles to gain a more profound comprehension of each process (Zheng et al., 2014; Gollakota et al., 2018; Ruiz et al., 2013).

Hydrothermal processing represents a fundamental thermochemical conversion methodology. The HTT process is gaining traction owing to its minimal processing temperature, remarkable energy efficiency, and the production of products with low oxygen content. (Ahmed et al., 2019., Peterson et al., 2008, Xiao et al., 2012). The process does not involve drying as a preliminary treatment; however, the resultant product exhibits a superior heating value, enhanced energy yield, and reduced ash content in comparison to pyrolytic char. Consequently, HTT is regarded as a more pragmatic option compared to the carbonization of animal manure to produce solid biofuel (Zhou et al., 2019; Song et

al., 2019). The fundamental hydrothermal process typically incorporates water as a reactant at a moderate temperature range of 250-374 °C, maintained under a pressure of 4-22 MPa (Ahmed et al., 2019). Under these circumstances, water assumes a role in a highly dense supercritical state (Yang et al., 2019; Gollakota et al., 2018). During this HTT process, organic material experiences many reactions, including depolymerization by hydrolysis, dehydration, and decarboxylation, resulting in the formation of water-soluble intermediates. Concurrently, many elimination, rearrangement, condensation, and polymerization processes may transpire, yielding water-insoluble compounds such as bio-crude and biochar (Posmanik et al., 2018). The hydrothermal process can be categorized into two distinct reaction conditions: subcritical and supercritical water conditions. The conditions are dictated by the critical point of water, which occurs at 374 °C and 22.1 MPa. The two parameters each present distinct advantages for the hydrothermal treatment of biomass (Kumar et al., 2010; Tran et al., 2016). Under supercritical conditions, the macromolecular structure of biomass undergoes decomposition, leading to the solubilization of significant portions of cellulose and lignin. At 100 °C, the water-soluble fraction of biomass undergoes diffusion into the water, while the hydrolysis reaction commences at temperatures exceeding 150 °C (Kor-Bicakci and Eskicioglu, 2019). The cellulose and hemicellulose break down to monomers and shorter chains during this process. The dense biomass transforms into a slurry during the intermediary phase at a temperature of 200 °C and a pressure of 1 MPa. Ultimately, the liquefaction process commences at a temperature of 300 °C, resulting in the production of crude oil. Consequently, the exploration of energy valorization of wet waste biomass via the hydrothermal method represents a significant area of inquiry in contemporary research (Yang et al., 2018). Hydrothermal pretreatment represents a promising approach for attaining significant solubilization of organic matter (Phuttaro et al., 2019). The effective and dependable pretreatment process dismantles the resistant structure of the lignocellulosic fraction, thereby augmenting both acidogenic and methanogenic biodegradability, which in turn enhances methane production (Deniel et al., 2016; Meegoda et al., 2018). Figure 2 below shows the structure change of lignocellulosic biomass during pretreatment.



**Figure 2.** Conceptual illustration of the disruption of lignocellulosic biomass by HTT (redrawn adopted from Ahmed et al., 2019).

Cellulose constitutes approximately 15-30% (on a dry basis) of the total biomass found in lignocellulosic materials, particularly in dairy manure (Chen et al., 2018; Kucharska et al., 2018). The cellulose chains possess a significant abundance of hydroxyl groups, which consequently facilitates the formation of hydrogen bonds among them. The development of microfibrils with high tensile strength in cellulose arises from the intricate interconnection of cellulose molecules through hydrogen bonding and van der Waals forces (Ahmed et al., 2019; Amin et al., 2017). Cellulose exhibits

a distinct orientation characterized by low amorphousness and high crystallinity. Consequently, the elevated crystalline index of cellulose and polysaccharide coating signifies a reduction in cellulose degradation (Kucharska et al., 2018). The primary objective of hydrothermal treatment is to alter the inter-intra hydrogen bonds, ultimately leading to modifications in the crystallinity structure of cellulose (Amin et al., 2017). Cellulose structural transformations via a degree of polymerization take place at high temperatures and pressures (Ahmed et al., 2018). Scattered literature supports the polymerization and cracking of cellulose during hydrothermal treatment (Xu et al., 2019; Fan et al., 2018). The hydrolysis behavior of both amorphous and crystalline cellulose has been examined (Hu and Ragauskas, 2012). Reduced temperatures were necessary to break the glycosidic bonds within the chain segments of amorphous cellulose, as increased crystallinity enhances their organization and stability (Kazem-Rostami et al., 2022).

Conversely, temperatures over 200 °C were required to extract glucose oligomers from crystalline cellulose during hydrothermal treatment (Hu and Ragauskas, 2012; Kucharska et al., 2018). Hemicellulose possesses a lower molecular weight and shorter chains than cellulose, making it readily hydrolyzable. The literature indicates that the significant breakdown of hemicellulose contributes to the generation of HMF as inhibitory chemicals. Elevated temperatures and extended residence time during acid treatment contribute to the development of inhibitors (HMF and furfural), which exert harmful effects on the fermentation process (McKillip and Collin, 2002). Limited research has been conducted on the ideal thermal processing of swine manure. The treated slurry at 70 °C exhibited a more favorable impact on biomethane generation compared to 110 °C (Rafique et al., 2010). In other studies, methane production increased at temperatures up to 140 °C with thermal pretreatment; however, as the temperature rose, biogas yield diminished. The ideal thermal pretreatment for agricultural waste was identified to be between 90 °C and 120 °C, resulting in a methane yield enhancement over 60% (Menardo et al., 2012). The hydrothermal technology for the treatment of lignocellulosic biomass has been thoroughly examined. Nevertheless, the appropriate hydrothermal pretreatment procedure for cattle (both non-dairy and dairy) remains under examination. Unlike unprocessed lignocellulosic biomass, which mostly comprises cellulose, hemicellulose, and lignin that have been degraded in the rumen's digestive tract (Nasir and Ghazi, 2015; McVoitte et al., 2019). Consequently, hydrothermal pretreatment at low temperatures is necessary prior to the anaerobic digestion process.

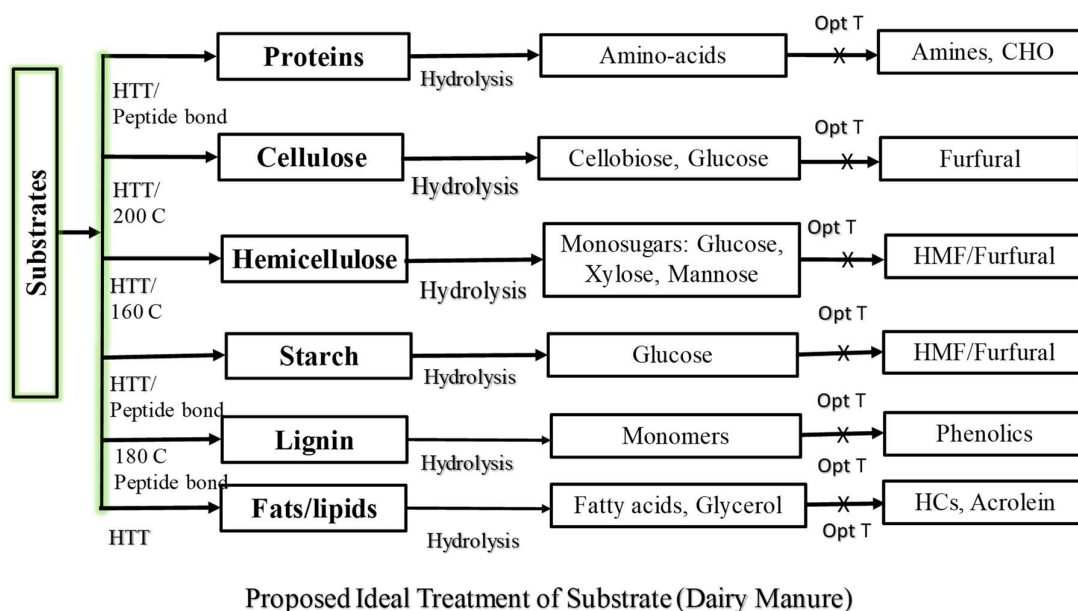
While hydrothermal processing of wet animal dung is not a cutting-edge approach, it presents certain obstacles. The primary challenges include generating inhibitory compounds that contaminate biomass, such as furfurals and 5-HMF. (Sayara et al., 2019; Ahmed et al., 2019). The D-glucose unit (cellulose) undergoes dehydration in supercritical water to yield 5-hydroxymethyl furfural, which is subsequently decomposed into formic acid and levulinic acid. The literature indicates that xylo-oligomers and oligomeric sugars can be eliminated through the hydrolysis and fermentation of pentose. Inhibitory compounds, including weak acids, furan aldehydes, and phenolic compounds, pose significant challenges to the enzymatic process and fermentation (Anukam et al., 2019). Researchers have employed metabolically engineered yeast strains to mitigate the inhibitory effects of these compounds (Ahmed et al., 2019; Zhang et al., 2025).

Additionally, lignin also inhibits the hydrolysis process by forming a physical barrier to the adsorption of cellulase enzymes (Paul and Dutta., 2018). Since the harsh hydrothermal pretreatment increases the lignin content in which de- and re-polymerization reactions occur, which is more inhibitory to cellulase than before treatment. Although thermal pretreatment has a lot of advantages, mostly in terms of digestibility, high temperature and long residence time prompted some chemical reactions such as the Maillard reaction, which forms complex (polymerization between the carbohydrates and amino acids) recalcitrance (Sanchis-Sebastia et al., 2019; Golon et al., 2014). Furthermore, the reduction in overall process efficiency, including methanogenesis, has been reported due to recalcitrant compounds. In the literature, it has been reported moderate pretreatment yielded higher methane (Ruiz et al., 2013). Therefore, it is crucial to determine the temperature and time for effective thermal pretreatment based on the characteristics of substrates. Furthermore, lignin-

derived phenolics are the main inhibitors of enzymatic hydrolysis (Ahmed et al., 2019). The biggest challenge to pretreating substrate (dairy manure) is combining the most appropriate technique that matches the ideal substrate composition.

Hemicellulose and lignin are solubilized at temperatures above 150 °C and 180 °C, respectively (Toor et al., 2011). The hydrothermal pretreatment process hydrolyzes hemicellulose by liberating acetyl groups and removing the lignin, which enhances the amount of cellulose fiber exposed. The detached hemicellulose remains in the liquid fraction of the pretreated slurry, and the formation of monomeric sugars during the process is minimal. To avoid sugar degradation and inhibitor formation, one should control the pH between 4 and 7 (Baruah et al., 2018; Li et al., 2014). Furthermore, the release of acetic acid during pretreatment acts as a catalyst to further degrade biomass and increase sugar yield simultaneously. Since the crystallinity of cellulose hinders the disruption of lignocellulosic material, size reduction is the usual step to disrupt biomass crystallinity (Baruah et al., 2018). However, more power input for mechanical size reduction, particularly in wet biomass, is not a viable option (Kucharska et al., 2018; Paudel et al., 2024). Hemicellulose is the least resistant to lignocellulosic materials' thermal and chemical processing components. Starch is also a standard component of lignocellulosic biomass, but it is more readily hydrolyzed than cellulose. The lipids (fats and oils) are non-polar compounds. These triglycerides and proteins are readily hydrolyzed in hot compressed water into fatty and amino acids via breaking ester and amide groups (Toor et al., 2011). Some other studies also showed that the hydrolysis of lipids is also autocatalyzed by fatty acids (Deniel et al., 2016). An initial pretreatment of lignocellulosic biomass (dairy manure) is necessary for the efficient progress in AD bio-refinery, such as during fermentation, etc. (Anukam et al., 2019; Putro et al., 2016). The main advantages of hydrothermal pretreatment are reducing the degree of crystallization, removing pathogens, and polymerizing cellulose (Putro et al., 2016). Overall, the pretreatment process includes the solids' fragmentation, alternating the lignocellulosic structure, increasing the contact area between the materials, and enzymatic reagents.

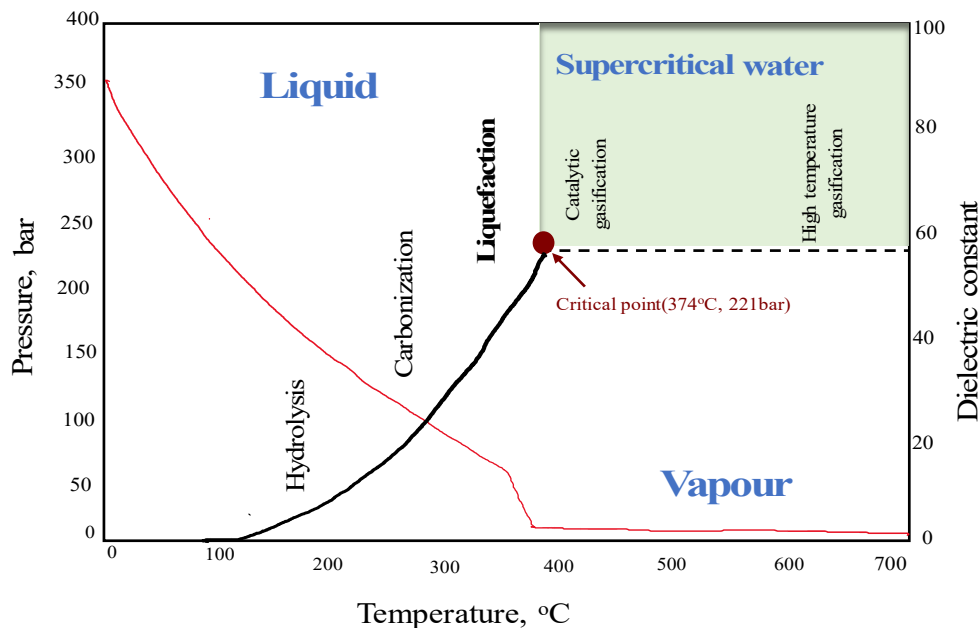
Considering all these facts, we proposed an optimum hydrothermal-processing technology for lignocellulosic biomass (dairy manure). The proposed hydrothermal pretreatment (as shown in Figure 3) is considered an environmentally friendly process. Figure 3 illustrates how the hydrothermal treatment at low temperature affects the composition of the manure structure. The structure of cellulose is characterized by extensive intramolecular and intermolecular hydrogen bonding networks, while proteins are linked by peptide bonds. The primary objective of pretreatment is to fractionate lignocellulose, thereby enhancing its accessibility for microbial degradation. Mild hydrothermal pretreatment results in the formation of fewer inhibitors, which arise from sugar degradation at elevated temperatures, and does not require chemical additives. Optimum hydrothermal pretreatment improves biodegradability, methane yield, and homogeneity by disrupting hydrogen and peptide bonds, sterilizing manure, and reducing pathogens. The diagram illustrates controlled hydrothermal pretreatment (Opt T), wherein inhibitory compounds, including amines, furfural, phenolics, and acrolein, can be effectively mitigated during the process. The development of cost-efficient technology remains a challenge.



**Figure 3.** Proposed optimum hydrothermal pretreatment of dairy manure.

#### 4.2. Water Chemistry During Hydrothermal Pretreatment

Understanding the hydrothermal reactions of cattle dung during hydrothermal processing necessitates an awareness of the role of water as a catalyst, reactant, and solvent (Kumar et al., 2018). Water typically has limited interaction with hydrophobic organic molecules under ordinary environmental conditions (20 °C and 1 bar). At the critical point, the reactivity of water escalates under increased temperature and pressure, both with and without phase transitions (Toor et al., 2011). In a supercritical state, water functions as both a reactant and a catalyst (Pavlovic et al., 2013; Tekin et al., 2014). At the critical state, the characteristics of water, including the ionic product, density, viscosity, and dielectric constant, exhibit rapid fluctuations (Ahmed et al., 2018). Consequently, at the critical point, water serves as an efficient medium for the majority of homogenous organic processes necessitating high miscibility. The absence of phase boundaries leads to rapid and complete responses during reactions. The dipole moment of supercritical water at this level is 1.85 D, functioning as a non-polar solvent. Likewise, the viscosity of water diminishes with rising temperature, approaching the viscosity of water vapor around the critical point. It enhances mass transfer, thereby expediting chemical reactions (Pavlovic et al., 2013; Tran et al., 2016). This low viscosity results in a high diffusion coefficient, thereby increasing reaction rates. Figure 4 illustrates that the dielectric constant of water is eighty under average temperature and pressure conditions. It decreases significantly to 5 at a critical point, which serves as the standard reference for non-polar solvents (Tekin et al., 2014). Furthermore, hot compressed water in both subcritical and supercritical states demonstrates notable physical and chemical properties, exhibiting behavior akin to that of gas and liquid (Ahmed et al., 2018; Kumar et al., 2018).

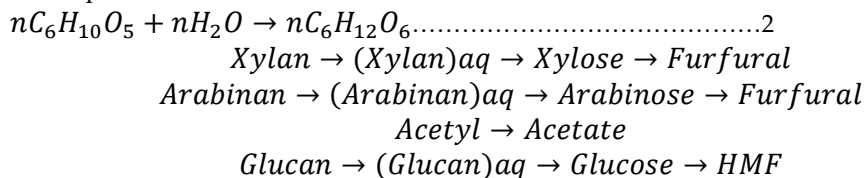


**Figure 4.** Phase diagram of water (redrawn and adopted from Tran et al., 2016; Wang et al., 2018).

The hydrothermal process in supercritical water has three basic stages: oxidative, hydrolytic, and hydrothermal. Water operates as an acid at high temperatures by auto-ionization, which produces hydrogen ions and causes the pH to drop significantly to an acidic level (Isikgor et al., 2015; Ahmed et al., 2018). Hydrothermal conversion of lignocellulosic biomass into glucose involves heating the biomass in conjunction with water (Kruse et al., 2013).

$$K_w = [H^+][OH^-]/[H_2O] \dots \dots \dots 1$$

The basic chemistry of the process involves adding water molecules and cleaving them at high temperatures into hydrogen cations (H<sup>+</sup>) and hydroxide anions (OH<sup>-</sup>), producing various forms of the original molecule. The stoichiometric reactions of cellulose and hemicellulose (xylan) to produce the equivalent glucose and xylose in the hydrothermal process are given below (Zhao et al., 2012; Ahmed et al., 2018). Overall, this is the typical hydrothermal process that converts biomass from a solid to a liquid.



Hydrous conditions are essential in the mechanism of hydrothermal pretreatment. Moisture content, temperature, residence time, heating rate, and catalyst are essential parameters in the hydrothermal process (Akhtar et al., 2011; Ahmad et al., 2018). Chemical reactions in high-temperature water adhere to ionic pathways, whereas low-density water operates via a free radical mechanism (Sandquist et al., 2019). Temperature plays a crucial role in providing sufficient heat to disintegrate organic macromolecules, facilitating fragmentation and the recombination of chemical bonds with high activity. Hydrothermal reactions are significant at elevated temperatures due to their high rates of degradation and polymerization of AD fiber compounds (Pelaez-Samaniego et al., 2017; Ahmed et al., 2018). The degradation of primary macromolecular constituents of sewage sludge was assessed in relation to temperature (Razavi et al., 2019). Polysaccharides exhibit a greater ease of hydrolysis compared to proteins, with lipids following in this regard. The kinetics of each component in AD fiber, being a complex mixture, are interdependent. Understanding the primary reaction pathways in hydrothermal reactions is essential. The efficiency of pretreatment is closely linked to

the characteristics and composition of the substrate, as each method presents distinct advantages and disadvantages. Hydrothermal processing appears to be a suitable option for various types of manure. The efficacy of this pretreatment is significantly influenced by the processing temperature and duration of pretreatment (Mcvoitte et al., 2019). Comprehending the water chemistry mechanism facilitates the development of an efficient pretreatment method that addresses the bottleneck occurring during hydrolysis, thereby optimizing the anaerobic digestion process.

Additionally, residence time is a significant factor in hydrothermal processing. Controlling the residence time influences the degree of polymerization of soluble monomers in the hydrothermal pretreatment process (Wang et al., 2018). An extended residence time enhances the degradation process. Literature indicates a critical residence time for achieving maximum oil yield (Pavlovic et al., 2013). Reaction times for anaerobic digestate range from minutes to hours (Awasthi et al., 2019). Pressure is an additional parameter influencing biomass degradation during hydrothermal treatment. Under subcritical and supercritical conditions, pressure facilitates the maintenance of single-phase media (Razavi et al., 2019). Increased pressure elevates solvent density, leading to the degradation of biomass macromolecules and facilitating decomposition and extraction processes. The literature has reported the influence of particle size in the HTT process. The liquid-to-solid ratio, or solid concentration, is related to the reactors. A higher liquid-to-solid ratio (LSR) is primarily utilized in continuous reactors, while a lower liquid-to-solid ratio is maintained in batch processes. The impact of particle size is minimal for elevated LSRs. Lowering the LSR for larger particle sizes results in reduced biomass solubilization. In certain lignocellulosic materials, reducing particle size is not required for optimal solubilization. Conversely, the reduction of particle size influences the recovery of polysaccharides (Sawatdeenarunat et al., 2015). Researchers have examined the hydrothermal pretreatment of cattle manure to enhance anaerobic digestibility (Wu et al., 2018; Font-Palma et al., 2019). Various structural and compositional characteristics influence the biodegradability of manure fiber, including cellulose crystallinity and the presence of lignin and hemicellulose (Elumalai et al., 2014). The pursuit of low-severity manure pretreatment that is both sustainable and economically viable will have a substantial effect on the anaerobic biorefinery.

#### 4.3. Effects of Hydrothermal Pretreatments on Cattle Manure

Most studies are performed on simplified model compounds rather than actual AD fiber. (Madsen et al., 2016; Deniel et al., 2016). The issues arise from the heterogeneity and complexity of anaerobic digestate. The morphological structure of AD fiber is a critical area of study. In-depth morphological studies would enhance the understanding of the physicochemical properties of AD digestate. Numerous studies have been utilized to visualize structural changes, primarily in model species of lignocellulosic biomass (Zheng et al., 2018; Madsen et al., 2016; Auxenfans et al., 2017). The prevalent techniques documented in the literature include Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (Wi, S. et al., 2015; Liu, H et al., 2013). The combined application of FTIR and NMR enhances the structural elucidation of the effects of pretreatment on fiber. Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) are employed to observe morphological alterations and to assess the crystallinity index, respectively (Pingali et al., 2016; Zheng et al., 2018; Elumalai et al., 2014).

Recent research has investigated hydrothermal pretreatment to assess its feasibility and practicality in anaerobic digestion bio-refineries for optimizing biogas production. The substrate includes a comprehensive array of simple and complex organic matter, and the identification of specific organic compounds through chemical analysis is instrumental in advancing technology in the anaerobic co-digestion process. The classification of biochemical composition is useful for assessing the biodegradability of substrates. A suitable pretreatment method can improve the anaerobic digestion of manure and increase methane yield (Maurya et al., 2015). (Niasar et al., 2011) studied the pretreatment mechanism using lime  $\text{Ca}(\text{OH})_2$  on cattle manure, showing 23% removal of total lignin and 76% higher methane yields than untreated manure. In other studies, pretreatment of

swine manure was studied to solubilize lignin degradation in manure, enhancing methane yield (Nizami et al., 2011). The alteration of structural disruption within the lignocellulosic matrix represents a complex process that is challenging to comprehend at the molecular level. The mechanism of xylan dissolution was investigated in the literature utilizing transmission electron microscopy to achieve an ultrastructural analysis (Wi et al., 2015).

Researchers have examined various pretreatment processes of dairy manure regarding structural changes (Miyata et al., 2018; Wei et al., 2015). Scanning Electron Microscopy (SEM) is employed to examine physical morphology, while Fourier Transform Infrared Spectroscopy (FTIR) is utilized to assess chemical composition. Nuclear magnetic resonance (NMR) and elemental analysis are employed to analyze raw materials and products (Ramirez et al., 2015; Miyata et al., 2018). The solid fraction obtained post-hydrothermal treatment exhibits a low yield due to structural modifications of cellulose and lignin. The solubilization of hemicellulose is directly influenced by temperature, resulting in a decrease in solid product yield as temperature increases. Carbohydrates exhibit greater susceptibility to elevated temperatures compared to proteins in lignocellulosic biomass. The elevated pretreatment temperature results in increased lignin content in the solid fraction, thereby reducing the overall methane yield (Fernández-Cegri, et al., 2012). The literature indicates the application of chemical pretreatment to solubilize the fiber content in dairy manure. Sulfuric acid effectively pretreats dairy manure to release monosaccharides from lignocellulosic material. Alkaline pretreatment, utilizing lime or sodium hydroxide, is extensively documented for the treatment of cattle manure (Ismali and Tinia., 2015). Thermal pretreatment has been applied to a mixture of cattle and swine manure for methane production. A 16% increase in methane yield was observed following the treatment of manure at 140 °C for 40 minutes (Ismali and Tinia., 2015; Mladenovska et al., 2006). A comparison of the thermal, chemical, and thermochemical pretreatment of chicken manure was conducted in other studies. Thermochemical pretreatment of poultry manure demonstrated a notable enhancement in methane yield (Ardic and Taner., 2005). Table 2 summarizes studies on the HTT process of dairy manure. This process signifies a potential method for the sustainable use of the valuable resource, dairy manure. Prior research has predominantly concentrated on hydrothermal liquefaction, carbonization, and gasification (Pavlovic et al., 2019). A limited number of studies have been conducted on the low-temperature treatment of dairy manure and other lignocellulosic biomass (Phuttaro et al., 2019; Song et al., 2019).

**Table 2.** Summary of major studies of hydrothermal processing (HTT) of dairy manure from the literature.

Manure type	Catalyst Condition	Reaction condition	Results	Reference
Dairy	NH <sub>3</sub> .H <sub>2</sub> O, H <sub>3</sub> PO <sub>4</sub> , glycerol (1%); Catalyst/manure=1:10 to 4:10	350 °C under N <sub>2</sub> for 30 min	Significantly increased the production of liquid chemicals.	Chen et al. (2018)
Manure Digestate and Food Waste	5 M H <sub>3</sub> PO <sub>4</sub> and 1 M NaOH	300 °C for 60 mins	Bio-crude oil yield (60 wt. %)	Posmanik et al. (2018)
Dairy Manure	CO is used as a process gas and sodium carbonate as a catalyst	Batch reactor, 250-350 °C, 5-20.5 MPa, 15 mins	67.6% oil yield	Theegala et al. (2012)
Dairy Manure fiber	Dilute acid hydrolysis (75%) H <sub>2</sub> SO <sub>4</sub> 3:5 sample to acid ratio	30 mins reaction time, 130 °C	84% yield of glucose	Liao et al. (2006)
Sewage sludge	N/A	Lab-scale reactor, Reaction time: 60 mins, 160 °C, 0.8 MPa etc.	methane yield (66%)	Gong et al. (2019)

Swine manure	0.1 M NaOH, H <sub>2</sub> SO <sub>4</sub> , CH <sub>3</sub> COOH	120 °C, 170 °C 600 ml high-pressure bath reactor, 1 h	94% extraction of phosphorous at 170	Epos, U. et al. (2016)
Goat Manure	NA	Fixed bed reactor, 500 °C Pyrolysis	26.1 wt. % bio-oil. 48.6% biochar	Erdogdu et al. (2019)
Dairy Manure	Ru	350 °C, 20 Mpa Batch, continuous flow stirred-tunnel reactor	CH <sub>4</sub> , CO <sub>2</sub>	Pavlovic' et al. (2019)
AD Fiber +Sewage Sludge	NA	Subcritical hydrothermal conditions (260 C), stainless steel autoclave	42% methane yield and significant oil contain (17,398 BTU/lb)	Elalami et al. (2019); Fox et al. (2019)
Cow manure and Wheat Straw	CoMo (2.8 wt.% Co and 10.3 wt.% Mo in Al <sub>2</sub> O <sub>3</sub> )	Continuous HTL, Co-HTL 330 °C	High Carbon yield of 34 and 38%, manure and wheat straw respectively	(dos Passos et al., 2023)
Dairy manure	NA	Two stage Hydrothermal treatment	Energy recovery (43.91-67.86%)	(Wu et al., 2023)
Swine manure	NA	Hydrothermal carbonization	High yield of biogas production (HTC+AD process)	Ferrentino et al., 2023)

## 5. Area of Concern Integrating Hydrothermal Treatment

The complexity of the anaerobic digestion system arises primarily from the interconnection of various process aspects, including microbiological, chemical, and operational factors (Cantrell et al., 2007; Font-Palma, C., 2019; Hagelqvist and Karin, 2016). The primary objective of the anaerobic digestion system is to optimize methane production. Enhancing the AD system necessitates a synthesis of methodologies, including hydrothermal processing (Shana et al., 2012). The available literature on hydrothermal processing studies is based on a laboratory scale (Cantrell et al., 2007; Chen J. et al., 2018). It is due to its simplicity of operation. Batch reactors are more common in the field of HTT. In the case of a batch reactor, any type of material can be screened with a wide range of operating conditions and process variations. On the other hand, batch reactors have some drawbacks, such as thermal instability (Castello et al., 2018). Since the process conditions are not constant, the system in batch reactors operates from ambient conditions to the desired temperature and pressure (Kumar et al., 2018). Because of the variation condition, the real mechanism is still unknown which parameter has a key role in the reaction. Also, in most batch experiments, the pressure is obtained by the heating up of the reactants, which correlates to the saturation condition of the water. To deal with this, the pre-pressurizing system with inert gas can help (Munir et al., 2018). Also, high pressure increases the solubility of the inert gas in liquid water, which makes pre-pressurization less useful (Ahmed et al., 2018; Putro et al., 2016).

The varying contact patterns associated with impellers in batch reactors present limitations for practical industrial application. The limitations, including prolonged heat-up and cool-down times, restricted heat recovery potential, constrained feedstock loading, and inadequate process control, present significant challenges to the adoption of this technology for future sustainability efforts. Consequently, batch processing is impractical for the industrial development process. Research must concentrate on ongoing experimental data and associated technical issues pertinent to this process (Castello et al., 2018).

## 6. HTT-Anaerobic Bioreactors Limitations

Conventional batch hydrothermal processing technology requires transformation into a continuous self-regulated process. Multiple research studies have been presented in the literature concerning continuous HTT (Ellitt et al., 2015; Yang et al., 2019). The studies examine laboratory-scale plants and the influence of pressure and temperature on the phase diagram, specifically the saturation line, as illustrated in Figure 4. However, limited research exceeds saturation temperature and pressure, among other factors. Two-stage and multi-stage continuously fed bioreactor systems are currently prevalent (Ahmed. F et al., 2018). In this system, biochemical processes including hydrolysis, acidification, acetogenesis, and methanogenesis can occur independently. The two-stage system appears to be an effective method for the treatment of all organic waste. Literature indicates that a two-stage system facilitates the selection and enrichment of distinct bacteria during each phase. Acidogenic bacteria convert complex organic materials into volatile fatty acids and alcohols (Rasapoor et al., 2020). Methanogenesis involves the conversion of substrates by methanogens into methane and carbon dioxide. Improvements to batch-related drawbacks can be achieved through the development of industry-scale continuous reactors (Atelge et al., 2020). The implementation of a continuous reactor can lead to significant improvements in mixing contact patterns. Researchers at the Pacific Northwest National Laboratory (PNNL) have recently focused on establishing continuous reactors for the processing of various biomass types. Currently, a novel approach for the development of lab-scale serial HTL devices is emerging in other regions (Ellitt et al., 2015).

Anaerobic digestion typically occurs within a sealed, self-contained reactor. This batch reactor facilitates regulated mixing and maintains a constant temperature in anaerobic conditions. The hydraulic retention time (HRT) in standard manure and municipal digesters typically ranges from 10 to 30 days. However, residence time depends entirely on feedstock types and solids (Meegoda et al., 2018). Additionally, In the US, complete mixed reactors (CMR), mixed plug flow reactor (MPFR), covered lagoon (CL), and plug flow reactors are getting popular in handling heterogeneous materials (Chapman et al., 2017). Anaerobic co-digestion is itself challenging organic waste treatment technology. It contains four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Meegoda et al., 2018). Therefore, a two-step AD process design helps to predict and control bioprocess and optimize the digestion system. Since an anaerobic reactor (digester) is also considered the heart of the digestion system, anaerobic microorganisms thrive and are responsible for digestion steps (Van et al., 2018; Meegoda et al., 2018). Some researchers categorized anaerobic digesters based on total solid contents, such as wet and dry types in literature. The solid content significantly impacts the AD process's cost, performance, and technique. The dry digesters usually intake feedstock having TS>20%. The wet digesters are categorized to serve the feedstock having TS <15%, which is well established in the wastewater treatment field (Van et al., 2018; Meegoda et al., 2018). Currently, because of the continuous progress of bioprocess engineering and biotechnology, the design and operation of new digesters are improving simultaneously. The effluents and wet biomass with high solid content can be well treated in continuously stirred tank reactors (CSTR), up-flow anaerobic sludge blanket (UASB) reactors, etc. (Hu, Y. et al., 2019; Neshat et al., 2017). Therefore, the design of bioreactors for the degradation of dairy manure plays a vital role in system performance.

### *Concerns and Challenges Related to HTT Before AD*

AD as a highly sensitive and technically complex process has its drawbacks including instability, long residence time, low efficiency, and highly polluted supernatant (Anukam et al., 2019; Amani et al., 2010). The reason for this is that the circumstances of AD and animal feed have a significant impact on the composition of manure fiber (Font Carolina et al., 2019). The anaerobic digestion process has four sequential steps, and the microbial activities associated with these feedstock pathways are difficult to anticipate at each phase (Sayara et al., 2019). Substantial investments and higher skill levels are necessary to maintain the process's efficiency. The utilization of chemicals and the excessive accumulation of specific compounds during digestion rapidly results in inhibition and failure (Amin

et al., 2017). While hydrothermal processing presents a promising alternative for extracting valuable chemicals from organic solid waste, it also entails numerous problems and issues. Hydrothermal processing efficiently addresses non-biological waste when alternative treatment approaches prove less effective (Ahmed et al., 2018). Hydrothermal processing possesses superior technical capabilities for waste reduction, hazards elimination, and resource recovery compared to all other alternatives (Yang et al., 2019). The hydrothermal conversion of solid waste into fuel is more time-efficient, requires less energy, and is more effective as it eliminates the need for the waste drying process (Kumar et al., 2018). Moreover, numerous obstacles are linked to the hydrothermal processing of diverse solid wastes. The heterogeneity of feedstock predominates the final products and yield, as the major components of feedstocks exhibit distinct behaviors during hydrothermal processing (Ahmad et al., 2018).

Autogenous pressure during the procedure aids in sustaining single-phase medium (Kim et al., 2014). It also enhances solvent density, allowing a high-density medium to penetrate effectively into the molecular structure of biomass components. Particle size, temperature, heating rate, residence duration, pH, and pressure are essential factors in biomass degradation during hydrothermal treatment (Sandquist et al., 2019). The literature has not examined the influence of critical reaction variables, including total solids, process temperature, solid-liquid ratio, and residence time, in hydrothermal treatment. Limited research has been undertaken on the various solid-liquid ratios (Gong et al., 2019). The aqueous state is crucial to the reaction mechanism of the hydrothermal pretreatment process. Water is an effective medium for heat transfer and storage (Ismail and Tinia 2015; Paul and Dutta 2018).

Addressing this issue requires a comprehensive analysis of reaction kinetics, reaction pathways, and the formation of various intermediates. It is essential to examine both parallel and consecutive reactions in hydrothermal processing. Hydrothermal treatment typically involves the evolution of various organic reaction pathways, making it crucial to identify these pathways (Pavlovic et al., 2013). A comprehensive understanding of reaction pathways requires the selection and production of numerous reactions and compounds to achieve the desired products. This process identifies the optimal synthesis route, facilitating environmentally sustainable and economically viable process design. Mass transfer is a critical parameter in the design and optimization of chemical reaction processes. Comprehending the mass transfer mechanism under intensified conditions, including elevated temperature and pressure, is essential. Manure possesses a complex chemical structure and elevated fat/lipid content, which restricts the effectiveness of the anaerobic digestion process (Hu. Y et al., 2019; Cantero-Tubilla et al., 2018; Bayat et al., 2019). Consequently, certain pretreatments are essential for a stable anaerobic digestion process. Furthermore, a detailed understanding of carbohydrate chemistry during hydrothermal pretreatment is essential for guiding sustainable anaerobic digestion bio-refinery processes. Conversely, limited research has been conducted on post-treatment for AD, which offers benefits such as low energy consumption and reduced digested volume (Yuan et al., 2019). This strategy additionally enhances the economic value associated with increasing methane yield.

## 7. Future Prospective of HTT on Anaerobic Digestion Technology

Recently, the usability and viability of anaerobic digestion methods have been on the rise. The hydrolysis phase constrains the anaerobic digestion of solid waste, necessitating ongoing research on an appropriate pretreatment strategy to enhance the solubilization of organic matter. Numerous pretreatment procedures have been examined on diverse lignocellulosic biomass, although only a limited number of ways have been suggested to attain elevated methane yield at minimal expense. Hydrothermal processing is an advantageous method for valorizing diverse biomass, particularly feedstocks with high moisture content. This method is garnering attention in anaerobic digestion biorefineries due to its ability to directly utilize high-moisture diverse wastes without requiring energy-intensive preparation. It is essential to examine model molecules and solid biomass substrates to comprehend the reaction mechanism and critical experimental variables. The distinct

physicochemical features of subcritical and supercritical water render the optimal temperature and residence duration crucial for the efficient treatment of diverse waste in the hydrothermal process. Hydrothermal processing integrated with anaerobic digestion bio-refinery will be implemented in industrial applications to address energy shortages and produce high-quality goods. The obstinate composition of dairy manure complicates the degradation of feedstock by anaerobic microorganisms in anaerobic digestion biorefineries. Consequently, optimal hydrothermal treatment is essential to improve the anaerobic digestion rate and methane production. The generation of recalcitrant inhibitors, such as furfurals and 5-HMF, during hydrothermal treatment can be mitigated following the experimentation with organic wastes. The ideal pretreatment technology must enhance feedstock digestibility, prevent inhibitor development, and be both cost-effective and environmentally sustainable.

The appropriate processing of livestock waste for biogas production has not been investigated to the same extent as other lignocellulosic biomass. Research on the impact of different pretreatment procedures on the lignocellulosic content of manure is limited. Nonetheless, novel characterization techniques are still required to address the inherent biodegradability of heterogeneous materials. The existing literature on dairy manure encompasses several research addressing economic and environmental strategies that restrict the efficient viability of the pretreatment process for its conversion into biofuel (methane). Subsequent investigations ought to concentrate on the response mechanisms of various pretreatment techniques and the relationship between the effective degradability of feedstock (dairy manure) and its compositional characteristics.

## 8. Concluding Remarks

From a managerial perspective, the anaerobic digestion of dairy manure is among the most innovative and prevalent technologies. The anaerobic digestion process generates sustainable biogas while mitigating prevalent adverse environmental and socioeconomic effects. The primary obstacle of manure for biogas production is its low biodegradability and minimal methane yield. To surmount these obstacles, cost-effective and eco-friendly pretreatment methods are required prior to anaerobic digestion that effectively decomposes organic materials. This review thoroughly addressed the challenges associated with hydrothermal chemistry and pretreatments. This debate indicates that low-temperature hydrothermal technology is an environmentally sustainable pretreatment for anaerobic digestion biorefineries utilizing dairy manure. A cost-efficient and ecologically friendly process has yet to be developed. The low-temperature thermal pretreatment procedure can be effective for the optimal usage of dairy manure.

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